OIL SPILLAGE STUDY
LITERATURE SEARCH AND
CRITICAL EVALUATION
FOR SELECTION
OF PROMISING TECHNIQUES
TO CONTROL AND PREVENT DAMAGE

to

DEPARTMENT OF TRANSPORTATION UNITED STATES COAST GUARD WASHINGTON, D.C.

November 20, 1967

AD 666 289

Government acceptance of this report does not imply concurrence with the results or recommendations set forth in the report.

PACIFIC NORTHWEST LABORATORIES
a division of
BATTELLE MEMORIAL INSTITUTE
3000 Stevens Drive
Richland, Washington 99352

Battelle is not engaged in research for advertising, sales promotion, or publicity, and this report may not be reproduced in full or in part for such purposes.

FOREWORD

This report summarizes research conducted by Battelle-Northwest for the United States Coast Guard under contract No. TCG-15560-A during the period 19 July 1967 through 19 November 1967. This program was conducted by a research team comprised of G. J. Alkire, Manager Chemical Sensors and Instruments; C. D. Becker, Research Scientist - Biology; M. W. Cook, Senior Research Associate - Chemistry; Diana Davis, Reference Specialist; C. E. Leach, Senior Engineer - Mechanical; G. B. Pauley, Research Scientist - Biology; P. L. Peterson, Engineer - Mechanical; W. A. Snyder, Supervisor of Reference; W. L. Templeton, Manager Marine Ecology; C. J. Touhill, Manager Water and Waste Water Research: and W. H. Swift, Project Manager.

Mr. D. P. Roseman, Naval Architect, Hydronautics Inc. was retained as consultant on aspects relating to ship design.

TABLE OF CONTENTS

1.0	INTE	RODUCTION	. 1-1	
	1.1	Background	. 1-1	
	1.2	Purpose of Study	. 1-1	
	1.3	Scope of Review	1-2	
	1.4	Study Organization	. 1-3	
	1.5	Structure of Report	. 1-4	
2.0	SUMMARY			
	2.1	Extent of the Study	2-1	
	2.2	Current State of Technology	2-3	
	2.3	Recommendations for Research and Development .	2-17	
3.0	PRE	EVENTION OF OIL SPILLAGE	3-1	
	3.1	The Design of Tank Vessels with Respect to Oil Spilla	ge 3-1	
	3.2	Operations	3-29	
4.0	CON	NTROL OF OIL SPILLAGE	4-1	
	4.1	Surveillance and Prediction of Slick Movement	4-1	
	4.2	Chemical Treatment Collection and Sinking	4-14	
	4.3	Chemical TreatmentDispersion	4-28	
	4.4	Biological Degradation of Crude Oil and Oil Fractions in the Ocean	4-44	
	4.5	Booming	4-47	
	4.6	Burning	4-56	
	4.7	Skimming	4-59	
	- 4 . 8 -	Treatment and Disposal of Recovered Slicks	4-65	
5.0		STORATION	5-1	
	5.1	Beaches	5-1	
	5.2	Rocky Coasts, Seawalls, and Structures	5-6	
	5.3	Restoration of Waterfowl	5-8	
6. 0		LOGICAL AND ECOLOGICAL EFFECTS	6-1	
0. 0	6.1	Oil Pollution and Fish and Shellfish	6-1	
	6. 2	Oil Pollution and Waterfowl	6-39	
	6.3	Oil Pollution and Aquatic Plants	6-58	
	6.4	Oil Pollution and Other Life Forms	6-74	
	6.5	Bioassay of Detergents	6-03	

7. €	RECOMMENDATIONS FOR RESEARCH AND DEVELOPMENT					
	7.1	General	l			
		7.1.1 Contingency Planning Activities	1			
		7.1.2 Oil and Other Hazardous Materials Information Center	2			
	7.2	Prevention of Oil Spillage	5			
		7. 2.1 Governmental and Regulatory Body Studies . 7-9	5			
		7.2.2 Maneuverability	5			
		7.2.3 Arrangement Modifications	8			
		7.2.4 Structural Studies	10			
		7.2.5 Mooring Gear and Ground Tackle 7-3	11			
		7.2.6 Safety Requirements	11			
		7.2.7 Cargo Containment, in Event of Collision				
		or Grounding				
		7.2.8 Radical Solutions				
	7.3	Control of Oil Spillage	13			
		7.3.1 Surveillance	13			
		7.3.2 Prediction of Oil Slick Behavior	13			
		7.3.3 Chemical Treatment - Absorption	15			
		7.3.4 Chemical Treatment - Dispersion	15			
		7.3.5 Biological Degradation	16			
		7.3.6 Booming	16			
		7.3.7 Skimming	17			
		7.3.8 Disposal of Recovered Slicks	17			
	7.4	Restoration	19			
	7.5	Effects	20			
8.0	ACKNOWLEDGEMENTS AND SUPPLEMENTAL CONTACTS 8-1					
	8.1	Acknowledgements 8-1	i			
	8. 2	Supplemental Contacts 8-2	2			

1.0 INTRODUCTION

1.0 INTRODUCTION

1.1 BACKGROUND

The increased size of tankers, density of materborne traffic, and offshore petroleum production operations strongly recommends attention to advance planning for prevention and control of oil spillage accidents, and for the development of defensive measures in the event accidents do occur. Statistical summaries (1) indicate that over 37 wt% of the 1,272.9 million tons (262.4 billion ton-miles) of United States waterborne commerce in 1965 consisted of petroleum and petroleum products. Tankers now on order, or in the design stage, have deadweight tonnages up to 312,000, and classification societies have conducted studies of 500,000 to 1,000,000 deadweight-ton tankers. Offshore production of oil on the United States continental shelf represented 2805 million barrels (2) in 1964 and is steadily increasing.

The TORREY CANYON (118,000 deadweight tons) disaster off Lands End, England, starting on March 18, 1967 and continuing for well over a month, demonstrated with dramatic clarity man's ability to pollute large expanses of the ocean and adjacent shores to an extent having international as well as large financial implications. Several excellent summaries of the TORREY CANYON disaster and subsequent activities have recently appeared. (3,4,6) Summaries of the immediate and nearterm biological and ecological effects have also been prepared. (7,8) This disaster also pointed up the lack of a well assembled body of knowledge and experience that could be applied. As a result, defensive measures were instituted largely on an "ad hoc" basis and in an atmosphere of emergency.

The study reported here is intended as a step toward assembling this body of information as a rational basis for future planning and action.

1.2 PURPOSE OF STUDY

The purpose of this report is to provide a literature review and evaluation of the current state of technology of prevention and control of major oil spillage on water, the restoration of the shore face and waterfowl, and the effects of oil pollution and defensive measures on aquatic life. The objective of this study was to assist in establishing

1) procedures and facilities for standardized control and cleanup based on current technology and experience and 2) areas where additional research and development could result in improved capability for prevention, control, and restoration.

1.3 SCOPE OF REVIEW

Specific areas of the study summarized in this report are as follows:

- Technical aspects of tank vessel design as related to prevention of oil spillage
- On-scene control of gross leakage
- Destruction or recovery of open sea oil slicks
- Disposal of recovered mixtures
- Protection of the shore face and estuaries
- Cleaning of shore face and estuaries
- Slick surveillance and behavior prediction
- Effect of oil pollution and treatment agents on marine flora and fauna
- Waterfowl recovery methods.

The above areas relate to oil spillage, regardless of origin, including both oil from tankers and from offshore production operations. Emphasis is placed on major oil spillage, although considerable information is included relating to small - scale, chronic oil pollution problems. These problems are particularly relevant to the biological and ecological effects, because much of the recorded quantitative information has resulted from studies of the small-scale problems.

This review and analysis is directed principally toward the technical aspects of oil spillage prevention and control and does not cover other considerations that may be equally or more important to the entire problem. This is particularly true in the area of oil spillage prevention. These other considerations include improved aids to navigation and navigational equipment, establishment of defined sea lanes comparable to those employed in air-traffic control, provision for shore guidance within a specified distance of land, application of speed restrictions (increasingly important due to the lessened maneuverability of large vessels), and

officer and crew training. Equally important are legal considerations as they relate to the rights of the threatened coastal state in the event of casualty in international waters: that is, the right to respond rapidly, uninhibited by possible rights of owners, salvors, insurers, etc.

Similarly, liability and compulsory insurance considerations can have an indirect but beneficial effect in prevention as well as providing for restitution. Salvage law enters both as it relates to operation of salvage equipment, regardless of flag, in territorial waters and as it relates to the liability of salvors in the event deliberate demolition or debunkering to the sea is necessary to limit the net overall consequences. Since these factors invariably involve international law, they are currently the subject of separate studies by the Intergovernmental Maritime Consultative Organization (IMCO) of the United Nations and by its members. (5)

It must be emphasized that a key element in any effort aimed at limiting the consequences of a major oil spillage incident will be the ability to rapidly respond with defensive measures. Therefore, contingency planning by government agencies and industry and the establishment of an early-warning and advisory system is of utmost importance.

1.4 STUDY ORGANIZATION

Search of the formal technical literature and supplementary contacts with academic and research institutions, industry, port authorities, and with local, state, and Federal agencies provided the base of information for this study. The review encompassed both United States and foreign information sources. In many instances, the supplementary contacts lead to further sources that were pursued to the extent time permitted. Although information of the biological and ecological effects of oil pollution and defensive measures is relatively well documented in the literature, it was apparent early in the review that the majority of the information relating to prevention, control, and restoration has not been published in the formal literature. In this regard, the supplementary contacts provided a wealth of valuable information, albeit often of a nonquantitative nature.

The assistance of the Office of Maritime Affairs of the Department of State was obtained in establishing information sources in Australia,

Canada, Denmark, France, Japan, Netherlands, Sweden, The United Kingdom, Venezuela, and West Germany. The Office of Naval Research, Branch Office, London, provided additional assistance in The United Kingdom. The National Oceanographic Data Center assisted in searching appropriate libraries in Washington, D. C. The Smithsonian Institution, Science Information Exchange, supplied summaries of Federally-sponsored research and development programs, and the National Referral Center for Science and Technology of the Library of Congress provided numerous fruitful contacts.

In a total of 360 supplemental contacts, 132 were with academic and research institutes, 78 with industrial firms, 54 with Federal agencies, 11 with state agencies, and 16 and 20 with various associations and port authorities respectively. Forty-nine contacts were made with foreign sources of information, including governmental, industrial, and independent organizations. Detailed listing of these contacts are given in Section 8.0.

Information obtained from all sources was reviewed by specialists in the appropriate discipline involved.

1.5 STRUCTURE OF REPORT

Figure 1.1 illustrates the approach used in this study in consideration of the problem of major oil spillage on water. The primary elements, essentially in order of occurence, are:

- 1. Prevention of spillage
- 2. Control or limiting the consequences of a spill once it has occurred
- 3. Restoration of the shore face and waterfowl
- 4. The effects--biological and ecological.

This general order is followed throughout this report. Section 2.0 provides a summary of findings and a brief statement of recommendations. Sections 3.0, 4.0, 5.0, and 6.0 provide the detailed review of available information in the areas of prevention, control, restoration, and effects respectively. Bibliographies of key literature or other sources are incorporated into each of the latter sections in recognition of the diverse needs and interests of the users of this report and the unwieldy nature of the bibliography covering the entire field of investigation.

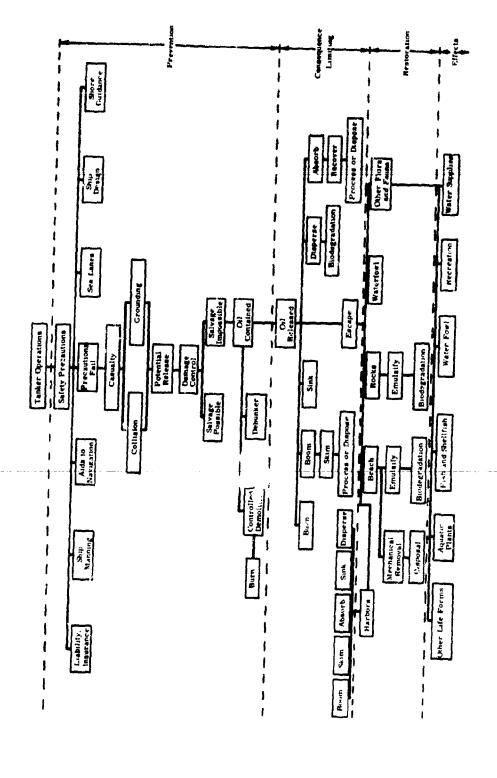


FIGURE 1.1. Sequence of Events

Section 7.0 presents detailed recommendations based on the current state of technology. Recommendations and rationale for future research and development in areas where appreciable gains can be anticipated are also given.

Section 8.0 tabulates the supplemental contacts made in preparing this review.

Literature Cited

- 1. Anonymous. Waterborne Commerce of the United States, Calendar Year 1965, Part 5, National Summaries. U. S. Army Corps of Engineers, Vicksburg, Mississippi. 1965.
- 2. Anonymous. Marine Science Affairs -- A Year of Transition.
 National Council on Marine Resources and Engineering Development.
 February 1967.
- 3. Smith, T. W. The TORREY CANYON Disaster, Annual Meeting of the British Association for the Advancement of Science, Leeds, England. September 6, 1967.
- Beynon, L. R. The TORREY CANYON Incident, A Review of Events, The British Petroleum Company, Ltd. September 1967.
- 5. Ashley, T. L., T. N. Downing, and H. Keith. Report on International Control of Oil Pollution--Report of a Congressional Delegation to the Third Extraordinary Session of the International Maritime Consultative Organization. Union Calendar No. 250. September 11, 1967.
- 6. Dudley, L. B. Harbourmaster's Visit to Cornwall to Study Anti-Oil
 Pollution Measures, Unpublished Report to Milford Haven
 Conservancy Board. April 25, 1967.
- 7. Glude, J. B. and J. A. Peters. Observation of the Effects of Oil from the TORREY CANYON and Oil Control Measures on Marine Resources of Cornwall, England and Brittany, France. Unpublished report, 33 pp. 1967.
- 8. Mercer, I. D., et al. "Conservation and The TORREY CANYON,"

 The Journal of the Devon Trust for Nature Conservation,

 Supplement. July 1967.

2.0 SUMMARY

2.0 SUMMARY

2.1 EXTENT OF THE STUDY

Information used to define the state of the art and present level of knowledge with regard to major oil spills has been developed in three major ways. First, a formal literature search was conducted using numerous library resources. Second, many personal contacts were made with governments, industries, universities, and individuals having detailed knowledge in the areas of prevention, control, restoration, and effects of major oil spills. Third, a more specific review of available information was developed by the technical contributors to this report based upon the formal literature search, personal contacts, and in some cases, unpublished and proprietary sources.

Over seven-hundred distinct literature citations were revealed by the formal literature search. The technical contributors found that the formal literature search was extremely comprehensive, and only in a few areas of peripheral importance were additional references subsequently developed.

The formal literature searches for information pertinent to the Oil Spillage Study were conducted primarily by the Battelle-Northwest and Battelle-Columbus technical information staffs, using their own technical libraries and external resources available to them. The University of Washington Fisheries and Oceanography Library, the Scattle Public Library, the National Referral Center for Science and Technology of the Library of Congress, the Smithsonian Institution Science Information Exchange, and the Defense Documentation Center of the Department of Defense were the major outside sources. The National Oceanographic Data Center provided literature reference service which included searches in the following libraries: Naval Oceanographic Office Library, Library of Congress, ESSO Production Research Library, American Meteorological Society Library, Geological Survey Library, Department of the Interior Library, Ocean Center (ASN-Research and Development), and the Corps of Engineers Library. Citations to reference material provided by the many supplemental contacts were, of course, also included in the bibliography.

The following index and abstract journals were reviewed for references to oil spillage literature:

Applied Mechanics Review, 1948 to present.

Biological Abstracts, 1940 to present.

British Technology Index, 1962 to present.

Bulletin Signaletique, appropriate sections.

Chemical Abstracts, 1940 to present.

Engineering Index, 1940 to present.

Geological Abstracts, 1954 to 1958.

Geophysical Abstracts, 1951 to present.

Geoscience Abstracts, 1959 to present.

Industrial Arts Index, 1960 to present.

Institute of Petroleum Journal Abstracts, 1940 to present.

Monthly Catalog, 1940 to present.

Monthly Index of Russian Accessions, 1955 to present.

Oceanic Index, 1964 to present.

Oceanographic Abstracts (Deep Sea Research), December 1966 to present.

Public Affairs Information Service Bulletin, 1955 to present.

Public Health Engineering Abstracts, 1952 to present.

Readers Guide to Periodical Literature, 1960 to present.

Technical Abstract Bulletin, Defense Documentation Center, 1957 to present.

Water Pollution Abstracts, 1955 to present.

Appropriate current periodicals (published during the past year) were reviewed for articles which have not yet been cited in the index and abstract journals.

As mentioned above, contacts made by the technical contributors have been incorporated in the bibliography.

2.2 CURRENT STATE OF TECHNOLOGY

2.2.1 Prevention of Oil Spillage

Tank Vessel Design Considerations

The major design and construction changes since World War II have generally increased the potential pollution hazards resulting from individual cases of collision and stranding.

Ship Size Increases. A consequence of size increase is a simple increase in the quantity of oil cargo potentially released in the event of collision or stranding. With tank vessel speeds essentially unchanged over the past 20 years, the energy to be absorbed in stopping the ship is directly proportional to the displacement, a quantity which has increased tenfold during this period. Further, the average speed of dry cargo and many special products carriers has increased from about 15 to 16 knots to well over 20 knots. On the credit side is the likelihood that a lesser number of collisions and stranding will occur as larger size tankers are built, replacing obsolete smaller tonnage tankers.

Arrangement Changes. For a given ship size, the adoption of tank lengths on the order of twice the tank lengths of 10 to 15 years ago, results in the following:

- Larger quantity of cargo release in the event of tank rupture
- Less probability of ship survival in the event of collision or stranding
- Less flexibility in control of cargo, i.e., simpler piping systems, fewer valves and controls, during normal operations as well as in the event of rupture of tank or piping.

The adoption of cargo lengths forming a greater proportion of ship length, while beneficial in the reduction of bending stresses, reduces, to some extent, the protection of cargo in the event of collision.

Hull Proportions. The trend toward designing for minimum values of LBP/Depth has necessarily increased the tendency toward greater drafts, particularly for ships in service from Persian Gulf to Europe and Japan, thus increasing the probability of grounding.

Bridge Location. The general trend toward locating the bridge aft has been a matter of some controversy. Some pilots maintain that the bridge amidships location is preferable from an overall navigation safety point of view. It should be noted, however, that events have demonstrated the aft bridge location to be a far safer place for crew members to be in the event of collision, explosion, or fire.

Structural Design. The elimination of wing bulkheads and the general reduction of tank vessel seantlings, based on more rational design procedures and use of protective coatings, results in the existence of less energy absorbing structure in the event of collision or grounding.

Machinery Simplification. The elimination of redundancy, while based on rational design practices, does necessarily reduce the ability to cope with emergencies to some degree. Specific examples are the installation of a single main boiler and reduced standby generator capacity.

Cargo Pumping. Simplification of cargo pumping systems reduces the flexibility in cargo handling and may limit the ability to meet certain emergency conditions. Particular examples are the elimination of stripping systems and adoption of the "Free-Flow" system.

Manning. The general reduction in manning levels may limit the remedial action which can be taken in the event of damage or fire.

Subdivision and Damaged Stability. Requirements for load line assignment and damaged-stability are more specific today than 20 years ago. However, with the reduced degree of subdivision, it is likely that modern tank vessels are less likely to survive certain types of collision and grounding damage.

Operating Practices

In recent years the major oil companies of the United States, through their shipping interests, have sought to reduce the most widespread and common source of persistent oil pollution on the seas: the overboard discharge by oil tankers and other ships of ballast water or tank cleanings containing oil. This reduction has been accomplished by prohibiting discharge of mixtures containing more than 100 ppm of oil into the sea at any time, even though the discharge of such oils is permitted by international convention in most areas of the oceans farther than 50 miles

from the shoreline. The waste or "slop oil" is collected after washing or deballasting the cargo tanks by decanting and is retained on board until it can be either discharged into special shore facilities for such oil or combined with the next load of cargo. Most refineries and some other terminals are now equipped with special slop oil receiving facilities. Combination of the slop oil with the next cargo is a procedure known as "Load-on-Top", and its usage as a method for preventing oil pollution is increasing. Many oil tankers are also equipped with some type of mechanical oil-water separator. Some of the newer, large tankers have separate compartments used exclusively for sea water ballast, which eliminates the possibility of oil pollution during deballasting.

To help prevent collisions, strandings, and danger due to weather disturbances, most oil tankers presently have considerably more than the minimum navigation instruments required by law. Recommended traffic lanes are being established in congested areas and improved weather and sea-state predictions provide advance warning of weather disturbances.

Various schools and training centers have been established to train ships officers. These schools specifically provide training in handling the latest large tankers.

Off-Shore Production

Offshore oil and gas drilling and production facilities, underwater storage tanks and pipelines, and shore-based processing facilities such as refineries are presently regulated by comprehensive state and federal antipollution and safety regulations which tend to keep oil spillage to a minimum. Ever increasing interest in good community relations has also helped curb wanton discharge of wastes.

Offshore oil wells and drilling operations are required to have such features as blowout preventers, storm chokes, fire prevention equipment, and aids to navigation. However, in the event of catastrophic failure of the various protective devices, several tens of thousands of barrels of oil could be discharged to the sea prior to shutoff.

Underwater pipelines and storage tanks are designed, constructed, and tested according to established safety codes. Pipelines are generally equipped with automatic valves that stop flow if a break in the line occurs.

Most refineries and unloading terminals are equipped to handle relatively small spills routinely, and many now encircle any operation where are oil spill could occur with a floating boom to reduce the spread of oil.

2.2.2 Control of Spilled Oil

Surveillance and Prediction of Slick Behavior

Aerial reconnaissance of major oil spills is far superior to any surface-based surveillance system. Large areas can be observed in relatively short periods of time, and the economies gained are significant. Presently, aerial photography, despite its obvious cloud-cover limitations, is the tool which can be most rapidly pressed into service. Black and white, color, and camouflage film are all readily at hand, and the methodology of their use does not require highly skilled scientific assistance. However, such assistance might be necessary in the interpretation of data.

More sophisticated techniques such as spectrophotometric, infrared, ultraviolet, radar, and microwave imaging are also available, but the higher level of sophistication requires the attention of skilled personnel for both operation and data interpretation.

Capability for prediction of oil slick behavior is not well advanced largely due to the great number of variables—all time dependant—involved. In general, slicks will be most strongly affected by wind conditions and can be expected to move at a speed on the order of 2 to 4% of the wind velocity and, in the northern hemisphere, slightly to the right of the wind vector. Little comparative information is available on the relative emulsification behavior with sea water of various crude oils and refined products, although this factor is important in predicting slick behavior.

Chemical Treatment--Absorption & Sinking Agents

The literature has revealed that there are numerous compounds and materials available to collect or to sink oil slicks. Four types of collecting agents have been identified as having been either demonstrated or suggested for oil slick recovery. These are: 1) floating absorbents such as straw and sawdust, 2) plastic or other polymeric materials such as polyurethane foam, 3) gelling agents, and 4) demulsifiers.

Most of the floating absorbents are inexpensive and can be readily disposed of by either burning or burial. However, recovery of oil values from these absorbents is not easily accomplished. The use of plastics or other polymeric materials, polyurethane in particular, although rather expensive, offers an excellent solution to the problem, since no residues are left on the ocean bottom and large quantities of oil can be reclaimed for subsequent use.

Gelling agents that can solidify petroleum materials are in the development stage and may prove helpful in collecting spilled oil.

Numerous solid absorbents for sinking oil are available. The weight of material required per unit of oil and the attendant logistics problem present practical difficulties. Demersal fish species may be adversely affected, and resurfacing of the oil mass is generally probable although it is delayed and slow. The method can be applied effectively in deep water, e.g., beyond the continental shelf and particularly in areas not involving commercial fisheries. It is doubtful, however, that it can be completely effective and probably will require back-up by other methods such as recoverable absorbents. The method cannot be recommended in shallow waters or in estuaries, particularly since the collection option can be readily applied in these instances.

In all cases, the spreading of absorbents, polymeric materials, gelling agents, etc., is materially aided when it can be accomplished by aircraft. However, experience has shown that greater degrees of success are apparent when the spill area is confined.

Chemical Treatment - Dispersion

A large number of dispersants and emulsifiers are available, although little quantitative comparative information exists. All such agents are toxic to aquatic life in some degree, but again, comparative data are scarce. The aromatic diluent solvent used with the majority of these agents may be the principal toxic agent.

Based on review of the aftermath of the TORREY CANYON incident, the majority opinion is against the general use of emulsifiers, either at sea or in restoration of the shoreline. This conclusion derives not only from the ecological considerations but also from practical

experience with detergents in the United Kingdom and France. However, this is a general conclusion, and specific instances may occur where detergents may be the best defensive measure. This may be particularly true in harbors where aquatic life is not a factor and where detergents can be employed under controlled conditions. Provision of effective agitation is a key factor in the efficiency and effectiveness of detergent emulsifiers. In general, physical collection is preferred if possible.

Biological Degradation of Crude Oil and Oil Fractions in the Ocean

Biological degradation of hydrocarbons in the ocean is controlled by environmental conditions such as nutrients, temperature, oxygen availability, degree of dispersion of oil in water, and species of microbiota. Although degradation will take place in the ocean, and is in fact the ultimate fate of oil, the rates are very slow. Recent speculation regarding the possibility of seeding oil slicks with microorganisms which feed specifically on the oil requires study to ascertain the appropriateness and potential for success of this method.

Booming

The ability to confine a spill in the area immediately surrounding the source is principally a function of time, availability of equipment, and prevailing environmental conditions. An incident that essentially opened an entire vessel to the sea would involve rapid spreading of the oil, and there would be little chance of containment equipment being effective unless it was in the immediate area and ready for use when the incident occurred. In a more probable case, where the oil release occurs over several days, the ability to confine the oil to the immediate area would depend largely upon the prevailing sea conditions. Booming in waters with a sea state greater than 3 is impractical ...th presently existing boom designs and even this is suspect if wind conditions are adverse.

For harbors and relatively calm waters, there are several commercially available booms which can contain a spill. Currents in excess of 1 1/2 to 2 knots make booming difficult without extensive skirts and anchoring systems. Supplementary means of confinement include coagulating the oil with such absorbing materials as straw, bark, or foamed plastics to prevent spreading.

There are two principle types of mechanical barriers applicable to oil spills: floating booms and underwater bubble barriers. Both are presently suitable only for relatively calm water and are subject to failure. Various types of floating booms are readily available commercially and have been used in harbors and other protected areas for many years. The floating boom is generally superior to the bubble barrier on an emergency basis because it is more portable and involves less erection time. A readily deployable bubble barrier could be developed however.

A permanently installed bubble barrier may be very effective for protecting restricted areas or around terminal facilities. The main advantage of a bubble barrier is the unrestricted entry and exit of ships; the main disadvantage is the complete loss of containment in the event of air supply failure.

Burning

The approach to cargo destruction on site depends largely on the nature and quantity of the cargo. If all attempts to salvage a vessel or cargo have failed and a ship has been abandoned, an attempt should be made to set the oil aftre while still contained within the vessel. Controlled demolition techniques may be applicable to opening the vessel without allowing oil escape while providing access of air. Mixing kerosene or other highly flammable material with a crude or heavy oil cargo would greatly enhance the burning.

Burning on the sea surface is not generally effective due to the rapid transfer of heat to the water, selective burning of the lighter fractions, and lack of oxygen supply except at the edge of a slick.

Skimming

Mechanical devices for collecting oil from the surface of the water such as rotating cylinders and suction pumps are generally available but have relatively small capacities. Furthermore their use is restricted to relatively calm waters to achieve reasonable efficiency.

Treatment and Disposal of Recovered Slicks

Technology presently exists whereby recovered oil slicks can be treated to any degree desired. Although such treatment is possible, the limiting constraint is either economics or environmental disposal standards. Improved techniques will evolve mainly through the economic incentives. For example, oil reclamation from recovered slicks has not been exploited. Reclamation is presently merely a function of expediency.

Treatment of recovered oil is likely to use techniques now employed by the petroleum industry in effectively dealing with wastewater effluents. These techniques are summarized below as sequential unit operations. The primary stage of treatment most often employed for oil-water mixtures is gravity separation where the lighter-than-water oils float to the surface and the larger solids settle. The most common device used is the API separator. Improvements that have been suggested are those that modify the skimming or oil collection system.

Most treatment plants which strive for a high degree of efficiency in the secondary stage of treatment of oil-water mixtures employ the following sequence of unit operations. First, alum or ferric salts are added to the wastewater. Lime is added when sufficient alkalinity for precipitation of the iron is not present. The wastewater is then gently agitated or flocculated to promote interparticle collisions for agglomeration. The resultant suspension is then allowed to settle in a sedimentation basin. In some cases where the oil content of the floc is high, flotation is used. This step is followed by filtration through a rapid sand-filter or through a multi-media filter.

While the secondary stage process described above is most often used, coalescence appears to be gaining greater acceptance for similar applications.

Biological treatment processes, such as activated sludge, trickling filters, aerated ponds, and cooling towers, are highly effective as a third or polishing stage of treatment. Experience has shown that the function of biological treatment as the last step prior to environmental discharge is highly appropriate.

Techniques for sludge disposal are few. The most common technique employed is to dewater the sludge by gravity drainage in soil, filtration, or centrifugation. However, care must be taken to avoid ground water contamination. The residue is either used as fill or it is incinerated.

In actual practice, many combinations of processes have been used. Once again, the degree of treatment is dictated either by economics or environmental disposal standards.

2.2.3 Restoration

Beaches

Several possible approaches have been taken in restoration of oil contaminated beaches. These include:

- Physical removal of the contaminated material
- Plowing under and covering with uncontaminated sand
- Detergent cleaning in combination with mechanical tilling
- A combination of the above.

In general, any procedure that applies to sand beaches can be extended to gravel or shingle beaches, only usually with greater difficulty.

Physical removal of the contaminated material with appropriate earth moving, snow plow, or farm machinery appears to offer the best solution. When the oil is relatively unweathered and hence mobile, addition of absorbing material such as straw, sawdust, or clay can greatly assist pickup. Timing of cleanup operations to correspond with a high tide can minimize the effort.

Plowing under is unsatisfactory because wave action ultimately causes resurfacing.

Detergent cleaning in combination with mechanical filling was used extensively following the TORREY CANYON incident on the coast of Cornwall. In retrospect, experience indicates that this method was extremely expensive, inefficient, and tended to diffuse the oil deeper into the sand.

It appears then that physical removal, with the assistance of absorbents as necessary and possibly backed-up by limited use of detergents, is the best method of restoration. A general recommendation that is applicable in all instances is not possible, and the best method or combination of methods must be decided on site.

Rocky Coasts, Sea Walls and Structures

Detergents were again extensively used in England in combination with high-pressure water hosing. Burning oil from sea walls was attempted with the only apparent cleaning achieved by spalling of the concrete surfaces.

Where equipment can be brought into place, steam cleaning with detergents can be effective.

Waterfowl

電影を下一きを見る中の一般のではは、このでは重要の一つのですが、ましてはありのでした場合のできませんまってい

Generally, attempts to clean large numbers of oiled birds--despite the humane merits--are futile. Of the many thousands of oiled birds captured and treated following the TORREY CANYON incident, a vanishingly small percentage ultimately recovered.

2.2.4 Biological and Ecological Effects

Fish and Shellfish

Small concentrations of many petroleum products and derivatives, as well as many detergents, appear to be highly toxic to fish and shellfish. Depending on the concentration, toxicity may correspond to the metabolic rates of the individual animals as related to their physiological state and various environmental conditions. With many of these toxic substances, fish and shellfish appear to react in a characteristic manner or to develop a specific pathological condition. In the natural aquatic environment, due to the diluting effects of the water, concentrations of toxic substances that would prove directly lethal to fish and shellfish are probably not always reached. However, there may be a myriad of subtle changes that escape the casual observer. These subtle changes may be more prominent during certain periods of the animal's life (emergence of fish fry, metamorphosis of crustacea, settling of shellfish larvae, etc.), or when environmental conditions are marginal for survival (low dissolved oxygen, extreme high or low temperatures, high turbidity, etc.).

There is a fairly abundant amount of literature concerning the concentrations of various petroleum products and detergents capable of causing direct mortality of fish under laboratory conditions, and the pathology that precedes their death. In contrast, there is less material dealing with the effects of these toxic substances on shellfish and crustacea and particularly the marine species of these animals. However, in many cases there are obvious difficulties in correlating laboratory experiments with existing natural conditions. The sublethal and more chronic problems that may develop from the use of various petroleum and detergent products have been examined only superficially. Such indirect effects warrant more detailed study before any categorical statement can be made concerning their overall action on populations of fish and shellfish.

Waterfowl

Pollution of water by various types of floating oil has disasterous effects upon individual species of waterfowl as well as upon large populations. The magnitude of these effects depends upon, among other factors, the amount and condition of oil released and the concentration of birds

present. Mortalities of oiled waterfowl representing many species are well documented. Apparently, the chances of survival of a contaminated bird are quite small. Exhaustion, starvation, and exposure are the readily evident results of oil contamination. Histopathological changes, which may be irreversible, are also associated with the ingestion of toxic oils. Non-toxic oils, although not directly lethal, appear to lower reproductive capacity when in contact with the plumage and eggs of birds.

Aquatic Plants

Crude oils and other products of petroleum may kill aquatic plants, primarily because of toxic constituents, if present in sufficient concentrations and over a sufficient period of time. Apparently, the extent of damage depends on the penetration of toxicants into plant cells. The effects are usually of short duration, unless exposure to oil is continuous or periodic, and recovery of the flora is generally rapid. In some cases, more luxurious growth of rooted plants may result because of the nutrients released from plant and petroleum decomposition. Growth of marine algae is often enhanced, since populations of invertebrates which normally graze upon them are reduced by the toxic substances. Detergents, and emulsions of oil and detergents, appear to be more toxic than oil alone to aquatic plants.

Other Life Forms

Oil pollution generally changes the species composition of bacteria present in the water so that forms utilizing petroleum or its various fractions as a nutrient source temporarily predominate. Many forms of bacteria multiply and are extremely effective in the decomposition of oil and various petroleum products. The enrichment of oil-contaminated water with bacteria and nutrients resulting from the decomposition of the oil frequently promotes 'he multiplication of protozoan--particularly the ciliates. These protozoa and also the released nutrients, in turn, are frequently beneficial to and stimulate many of the higher forms of aquatic life. The presence of oil films on the surface does not, under usual natural conditions, reduce the amount of dissolved oxygen present in the water sufficiently to damage most aquatic organisms.

Many detergents are harmful, depending primarily on concentrations, directly and indirectly to bacteria, protozoa, and other microscopic and

macroscopic organisms in the food chain leading to the development of higher vertebrates and invertebrates. Most detergents, but not all, are ultimately decomposed by bacteria.

Injury to macroinvertebrates from oil may issue directly (smothering, clogging of feeding mechanisms) or indirectly (tissue irritation, destruction of vital food organisms). In most cases water soluble fractions released from the oil are responsible for the damage. Toxic components are usually more volitile or soluble and are lost quite rapidly; the unsightly residues are less damaging. Deposits of oily sludge on the bottom, however, may smother and otherwise damage sessile, benthic dwelling forms.

Many detergents, and emulsifications of detergents and oil in water, are toxic to aquatic life. In most cases, their toxicity exceeds that of oil alone. The most spectacular losses of intertidal marine organisms occur not from oil, but from the widespread application of detergents used to remove the oil.

Populations destroyed by oil and emulsifications are fairly rapidly restored by natural biological processes, provided that exposure is not continuous or periodic. The rate of repopulation depends on the reproductive capacity, fecundity and growth rates of the affected species, as well as by the dilution, decomposition and disappearance of the destructive principles.

2.3 RECOMMENDATIONS FOR RESEARCH AND DEVELOPMENT

Recommendations for research and development activities are briefly summarized below. Detailed discussion of these recommendations and their rationale is given in Section 7.0.

2.3.1 General

- 1. Establish a hazardous cargoes information center to provide the technical basis for cargo classification and licensing as well as for continuously updating technology for prevention, control, and restoration and for prediction and analyses of effects.
- 2. Establish contingency plans on an area basis in cooperation with local governments and industries. These plans should include establishment of a warning network and the training of personnel. The contingency plans should include other hazardous cargoes as well as oil and should include careful analysis of the environment and the resources potentially threatened.

2.3.2 Prevention

- Study the backing characteristics of existing vessels, particularly with respect to known casualties.
- Establish standards defining acceptable values of ahead reach and time to execute the crash stop maneuver, as measured on standardization trials.
- 3. Study the effects of propeller type on stopping characteristics.
- 4. Study the relative characteristics of various transmission systems.
- Study auxiliary braking devices such as shaft brake and hydrodynamic systems.
- Study the maneuvering characteristics of existing ships with particular reference to casualty records.
- 7. Establish minimum standards for control, including turning rate and turning circles as determined by standardized trials procedures.
- 8. Study improved rudder designs.
- Study the applicability of thruster design to augment steering systems for large tankers.

- 10. Evaluate the benefits of structural barriers on the ship's sides.
- 11. Study the relationship of permissible wing cargo tank length and ship location with respect to damage probability and limiting potential cargo loss.
- 12. Establish minimum distance of the cargo tank section forward bulkhead from the forward end of the ship. Establish a minimum number of bulkheads between stern and cargo tanks to provide a minimum standard of collosion protection.
- 13. Study the feasibility of double bottoms, particularly inboard of the longitudinal bulkheads.
- 14. Establish standards for bridge visibility in terms of line-of-sight over the bow.
- 15. Continue the study of longitudinal bending and improvement of estimating methods with continued rational development of minimum standards.
- 16. Study the consequences of general scantling reductions.
- 17. Study modifications to structural design to increase collision protections, such as outboard wings to absorb collision energy and limit penetration.
- 18. Evaluate potential gains from use of higher strength steels.
- 19. Evaluate the permanent installation of stress measuring instrumentations at strategic locations in the hull structure with indicators located on the bridge.
- 20. Develop more rapid means for release of anchor and chain.
- 21. Study problems involved in the use of bow anchors in association with large bulbous bows.
- 22. Study the advisability of requiring the fitting of stern anchors as an emergency stopping and maneuvering device.
- 23. Establish mandatory inerting requirements for normal use as well as for emergency measures.
- 24. Study cargo pumping methods and piping systems with the objective of establishing mandatory emergency cargo pumping systems.

- 25. Study the need for emergency power sources to permit limited capability for cargo pumping in the event of loss of the main plant.
- 26. Develop a simple draft-determination system.
- 27. Evaluate the installation of visible signals to complement audible whistle signals.
- 28. Evaluate the possibility of requiring the carrying of inflatable or other types of oil booms which would be secured to the ship in an arrangement to contain the oil slick.
- 29. Evaluate the possibility of requiring the carrying of dispersion and sinking agents.
- 30. Develop foamed plastic systems which could be released to temporarily seal off small ruptures in cargo tanks.
- 31. Evaluate the possible restriction of oil tanker operation to remote or lightly travelled routes.
- 32. Evaluate the economics and benefits of installing costly navigation and/or inertial-guidance systems for more precise control of ship routes.
- 33. Study the use of advanced demolition and pyrotecnic devices to enable sustained combustion of oil aboard ship in the event salvage is impossible.

2, 3, 3 Control

Surveillance and Prediction of Slick Movement

- 1. Evaluate potential of photographic, infrared, ultraviolet, radar, and microwave imaging for slick detection.
- 2. Evaluate filtering systems which would give greatest oil-water contrasts.
- 3. Evaluate, in depth, the all-weather capability of a microwave and radar imaging system.
- 4. Evaluate magnetic tape systems for the collection and processing of data from imaging systems.
- 5. Develop improved capability for predicting the movement of oil slicks as a function of environmental conditions.

Chemical Treatment - Collecting and Sinking Agents

- 1. Develop a standard evaluation technique to assess the effectiveness of collection and sinking agents.
- 2. Evaluate effectiveness of absorption of measures in terms of time, materials, manpower, and dispe. of problems.
- 3. Develop economical absorbents which mee predetermined criteria as defined in recommendation 1.
- 4. Evaluate the possible confinement of oil spills by hydrophilic agents.

Chemical Treatment - Dispersion

- 1. Develop a standard evaluation technique to assess the effectiveness of chemical dispersants including toxicity to m. ine organisms.
- 2. Explore the possibility of developing a non- or low-toxic emulsifier.
- 3. Study improved means of detergent application including agitation.

Biological Degradation

- 1. Evaluate and demonstrate the use of specific microbial species for accelerating oil degradation. Evaluate and demonstrate the use of mixed cultures for the same purpose.
- 2. Evaluate methods for enhancing oxygen availability and nutrient supplies for accelerated oil degradation.
- 3. Evaluate the mechanisms of anaerobic degradation of sunken oil masses.
- 4. Evaluate the potential toxicity of intermediate products of both aerobic and anaerobic degradation.
- 5. Evaluate the effects of oil dispersion on accelerated biological degradation.

Booming

- Develop a standard technique for evaluation of candidate boom systems.
- 2. Develop improved boom designs based on careful analysis of the hydrodynamic, aerodynamic, and deployment factors involved with the objective of achieving capability in rough water.

- 3. Specifically, explore in detail the optimization and efficiency of bubble-curtain boom systems either for fixed installation or for temporary deployment.
- 4. Further evaluate the use of "chemical booms" for slowing the spread of oil; e.g., peripheral gelling agents.
- 5. Explore the potential for a "suction boom" capable of continuous removal of oil accumulating along the face of the boom.

Skimming

1. Develop an improved oil skimming vessel based on incorporation of several techniques currently employed separately: use of hydrophobic plastic absorbents in combination with drum type skimmers. The specific objective will be to achieve capability in unsheltered water.

Disposal of Recovered Slicks

- 1. Investigate improved methods for the disposal of oil-containing sludges.
- 2. Investigate methods for improving oil reclamation in the disposal of recovered slicks.
- 3. Develop improved incineration systems for disposing of recovered slicks.

Restoration

 Conduct field tests of the alternate methods for beach restoration including the behavior, with time, of oil on a beach and its removal by direct physical means or assisted by absorbents or detergents.
 Several mechanical removal methods should be evaluated.

Effects

- 1. Develop more comprehensive data than is presently available to redefine standards of quality for water polluted by petroleum products and detergents under chronic, low-level situations.
- Develop accurate short-term tests for measuring acute toxicity.
 Develop accurate long-term tests for measuring chronic toxicity.
- 3. Establish standardized bioassay techniques which would permit comparison between geographical and ecological regions.

- 4. Develop data on the degree of tainting and rate depuration for fish, shellfish and crustacea.
- 5. Study the economics of mass transportation of selected shellfish brood stocks to clean areas for immediate repopulation of depleted areas.
- 6. Examine the clinical response of aquatic organisms to different sublethal concentrations of petroleum and detergent products.
- 7. Define under experimental conditions the physiological parameters (respiration rate, photosynthetic activity, metabolic rate, growth rates, metamorphic change, etc.) for aquatic species subject to oil pollution.
- 8. Study biochemical parameters which relate alterations in metabolic processes with changes ultrastructure of the cell.
- 9. Use field studies to evaluate acute and long-term exposure in natural conditions and relate these to laboratory findings.
- 10. Evaluate ecological consequences of sunken oil-absorbent masses, and define areas where adverse ecological effects of such masses are likely or unlikely.
- 11. Evaluate the effects of floating or sinking oil on pelagic eggs and larvae of marine organisms, particularly fish and shellfish.
- 12. Study the ecological factors affecting the natural repopulation of inshore areas depleted by oil or oil and detergents.
- 13. Experimentally determine the effects of oiled plumage on the nesting success of waterfowl.

3.0 PREVENTION OF OIL SPILLAGE

3.0 PREVENTION OF OIL SPILLAGE

3.1 THE DESIGN OF TANK VESSELS WITH RESPECT TO OIL SPILLAGE

3.1.1 Introduction

The stranding of the TORREY CANYON and the consequent uncontrolled release of thousands of tons of polluting oil cargo provided the impetus for the initiation of studies of means for the prevention of such catastrophies. The government and public alarm associated with this particular maritime disaster, with the attendant pollution of English and other European beaches, arose with the realization that many tankers exceeding 100,000 tons deadweight capacity are currently operating on the world's oceans. Further, in addition to the trend toward larger vessels, the total tonnage of petroleum and similar products being transported in international waters is many times the quantity carried during the period immediately following World War II.

Proponents of the large tankers note that their widespread use results in a need for fewer ships in operation, thus reducing the probability of tanker collision and stranding. Nevertheless, the greater world consciousness of conservation requirements, and a recognition of the implications of future disasters like the TORREY CANYON disaster, has led to intensified study of the many facets of tank vessel operation. Some related discussion is included in References 1 through 7.

Therefore, this brief review is directed toward a consideration of tank vessel design and its implications with respect to gross pollution resulting from collision or stranding. It is recognized that pollution may result from less spectacular sources, including the indiscriminate discharge of oily ballast and the slow release of liquid cargoes from sunken tankers, particularly the mass of ships sunk during World War II. These sources of pollution are the subject of intensive studies elsewhere and will not be considered here.

This study has relied heavily on the background of the reviewer in preliminary design, particularly of tank vessels, the technical literature, and direct discussions with representatives of the U.S. Coast Guard.

The American Bureau of Shipping, The U.S. Salvage Association, and elements of the shipbuilding and tanker operations industry.

3.1.2 Tank Vessel Design History

General Considerations

For purposes of this review, the tanker design evolution is assumed to start with the 16,000 deadweight-ton T2-SE-Al tanker of World War II. This design, in series production in the United States during and immediately following the war years formed the backbone of much of the world's tanker fleet for many years. Many T2 tankers are currently in operation in their original configuration, and many exist as the result of many "Jumbo" conversions. The higher powered "Mission Class" T2-SE-A2 versions of this class form a significant portion of the MSTS and U.S. Navy oiler fleet.

With the exception of the steam turboelectric main propulsion machinery and electric drive cargo pumps, the T2 tanker is, in general arrangement, a parent of the tanker designs developed during the early postwar years. Typical characteristics of these vessels include:

- Cargo section divided by a pair of longitudinal bulkheads into port, center, and starboard tanks
- Relatively short cargo tanks, on the order of 40 ft in profile, regardless of ship size
- Provision of poop, bridge, and forecastle superstructures with navigating bridge located amidships
- Provision of forward and after fuel bunkers
- Provision of forward and after pump rooms
- Relatively long, single screw, main propulsion machinery, with separate boiler and engine rooms.

Characteristics of American flag ships of this period are well described in two extensive papers given before the Society of Naval Architects and Maritime Engineers in 1960. (28, 29) The range of sizes extends from 18,000 dwt (deadweight ton), to the 25,000 dwt "supertankers," to the 106,000 dwt MANHATTAN. The characteristics listed above are generally typical of these ships. The one outstanding exception is the MANHATTAN, fitted with twin-screw main propulsion machinery with a total output of 43,000 shp (shaft horsepower). This ship is the highest powered tanker in existence today.

Table 3.1-1 contains a comparison of principal characteristics of a representative group of U.S.-built tank vessels including the basic T2 tanker, of the postwar to 1960 period. This table is in no way meant to be comprehensive, and a large number of intermediate ship sizes, and the many foreign built tank vessels, are not included.

A unique phenomenon in tanker construction, still very much a part of the current shipbuilding scene, was the development of the "Jumboizing" process in the early 1950's in the Baltimore yards of the Maryland Shipbuilding and Dry Dock Company and the Bethlehem Steel Co. In general, this procedure involved the joining of the stern of an older tanker, typically a T2, containing the propulsion machinery and after quarters, to a new, larger, cargo section. In this manner, the uneconomic surplus T2 tankers, frequently including wasted original cargo sections, were converted to larger hulls approaching 30,000 dwt. "Jumboizing" is not limited to T2 sterns, and this procedure has been applied to parent bulls as large as 60,000 dwt. The most celebrated case is that of the 118,000 dwt TORREY CANYON, formed by a union of the stern of the original 67,000 dwt U.S. flag tanker TORREY CANYON and a new forebody.

From the late 1950's until the present, tanker design evolved through a number of important changes, all directly related to reduced cost of construction and operation. These changes include increased ship size, reduction in complement, simplification of tank and cargo pumping arrangement, and changes in traditional ship proportions. These developments, and their implication with respect to collision and stranding, are discussed in the following paragraphs. Typical characteristics of this most recent group of tankers, developed from the late 1950's to the present, are included in Table 3.1-2.

Size and Speed Increases

The need for very large tankers, well in excess of the largest then in existence, developed as a direct result of the Suez Canal closing during the Arab-Israeli conflict of 1956. It had become clear earlier that large tankers, in excess of 100,000 dwt capacity and too large for Suez Canal transit in loaded condition, could operate from the Persian Gulf via the Cape of Good Hope to Europe at less cost than tankers designed to the

TABLE 3.1-1. Representative U.S. Built Tankers--World Warll to 1960

,																	
MANHATTAN 101,000	Meshirdr m	. O. SCH	132.0		49" 1 1/2"	137, 200	18, 695	900 91:	=	: 2			41, mag (T/53	17 1/2	# 64	13, 25	£
PRINCE SE SCOTTE TO SEE	Bertisteneren		.0.511	•	44, 1/3,	30.30	71, 300	586.540		: :		. i.	# # # # # # # # # # # # # # # # # # #	16 1/2	1.11	13.61	=
SANGKENA SG. 600	Neugaurt Neus Bertalemen	710.0		.0		17, 606	69, 608	476, 800		: 2			25, 25	17 1/2	9	12.63	z
WOMLDBEAUTY & CLASS 44, 600	Bethlehem	705. 6"		. o. e.	37' 10"	55, 900	46, 000	395, 000		: :		.0.0	15,000	2		14.1	**
ESSO CETTYSBURG 35,000	Newport News	.0	.0.66	4.7.	36. 4.,	50.180	37. 180	317, 700	2	. 2	:o •			=	1.31	14.1	\$
CTTIES SERVICE BALTINONE 31,000	씸	.0.019		46. 3	33. 11 1/3"	42, 790	32, 650	273, 000	22				15, 800	16 1/2	8.1	13.4	95
3AHRA 28,000	뫮			.0.++		36. 650	34, 250	241, 500	2	·	.0.07	40.0	13, 750	161/2	7.0	13.5	 3
P. C. SPENCER 25,000	8	\$75. 0	78. 0.	44. 2 3/4		32, 760	15. 200	212.4	•	•	. 0		13, 750	11	7.37	13.0	Ì
OLYMPIC CAMES 16, 600	Berhiebern	.9.54.		31.6"	2		18.	152, 206	=	•	7.35	36.6"	7, 700	2	1.1	•	;
17-5E-A1	Versons	.0 .003	.0.49	39. 3.	30, 1	21.8	16, 770	141, 900		_•	.9.90	36. 6"	£. 600	14 1/2	• •	12.4	
Kome Komingi det	Besider	Langth, BP	Breach, mid	Depth. mid	Draft, mid	Diaplacement Total, tone	Description Total, 1000		Kumber of Wing Tanks	Number of Center Tanks	Length of Wing Tests	Langth of Center Tanks	ећр. технитет 6. 600	Sustained See Speed, knots	L.BP/Bresoth	Length; Depth	Cre

1 ABLE 3.1-2. Representative Modern Tankers--Late 1950's to Present

ACCORDED TO THE CONTRACT OF TH

1

THE RESIDENCE OF THE PARTY OF T

Numinal day	VALLIA FORCE CLANS 36, 000	SINCLAIR TENAS 47,000	C7/2 C32/ W31	PONECAWA MARE FL 000	ST. MICHARLS 76, 900	TORBEN CANYON 118, 000	10MYO MARE	MART	ļ
Vard. Nationality	Bethlehem (U.S.)	Pethieren (1.8.)	•	Fupun		W. N. A. Japan	Japan	Fapan	urdi.
Length, BF Breadth, mid Depth, mid Draft, mid	630° 0° 48° 4° 48° 4° 48° 4° 48° 4° 48° 4° 48° 4° 48° 4° 48° 48	105' 0 102' 0 50' 0 38' 2 1/2	116. 0" 14. 4. 4. ". ". ". ". ". ". ". ". ". ". ". ". ".	108°3° 47°3° 45°3°	783' 11 1 · B" 123' 10" 55' 5 1/4" 40' 6"	936' 4" 125' 0" 68' 7" 58' 4"	15 17 40 15 50 80 15 17 17 52 15 15	1631 4 1/2" 1631 4 1/2" 1611 1/4" 571 1610/4"	1042' 3" 174' 10 1·2" 105' 0"
Dusplacement Total, tons	44, 000	59, 800	1	!	91, 750	į	179, 600		
Total tons	34. 000	47, 700	66, 100	73, 415	76, 270	114,000	150,000	2 MS. 60g	
Cargo Capacey, barrels Number of Wing		3.45, 000	582, 800	3h6, 000	604, 000	-	1. 200, 900	1, 540, 680	ļ
Tanks Number of Center Tanks	9 . 7	7 = 2	# .4	9	<u> </u>	21	0.	9	1
Length of Wing Tanks		40, and 80,	!	-	 	.0.501	•	•	1
Length of Center Tanks	L	., 0 .9+	1		1	.0.601		}	ļ
Alle maximum Sustained Sea		15.000	13, 000	14, 000	207, 050 bby	75, 500	30, 000	38, 600	77, 400 (T.)S)
Speed, anota	<u> </u>	<u>.</u>	ŗı	=	2/191	*	9/1 91	16 1/4	
tulal annu	3 7	;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;;	14.0	11.2	6.34	7,49	6. 11 12. 55	2 3	N (
į	33	-	2.5	£ 15	13	1	2.9	,	

canal limitations. In April 1967, 51 ships of over 100,000 dwt capacity were on order. The trend has increased to capacities in excess of 200,000 dwt. Characteristics of the largest tanker currently in service, the 206,000 dwt IDEMITSU MARU, as well as the larger Shell and Esso tankers currently under construction, are summarized in Table 3,1-2. Among the largest tankers known to be under construction today are six, 276,000 dwt capacity ships that will have the following characteristics:

Length, overall	1135 ft
Length, between perpendiculars (LBP)	1082 ft 8 in.
Breadth, mld	174 ft 10 1/2 in.
Depth, mld	105 ft
Propulsion	34,700 shp, twin
	screw, steam turbing

Six 312,000 dwt vessels are known to be under contract to Japanese yards for National Bulk Carriers.

The question of practical limits to tanker size has been considered seriously by shipping authorities, and the various classification societies have conducted serious studies of 500,000 to 1,000,000 dwt tankers.

Lloyd's, Det Norske Veritas, and the American Bureau of Shipping studies have established the feasibility of building ships to 500,000 dwt. Specific dimensions of ships to 1,000,000 dwt are given in References 56,57 and 61. Study results by Lloyd's, Det Norske Veritas and others have produced the approximate characteristics given in Table 3.1-3.

TABLE 3.1-3. Projected 400, 000 dwt to 1, 000, 000 dwt Tankers

Study by	Lloyd's	Det Norske Veritas	Mitsui Shipbuilding & Engineering Co.
Length, ft	1, 300	1, 246.7	1,190
Breadth, ft	225	218.2	204
Depth. ft	112	106.6	110
Draft, ft	80	85.9	80
Displacement, tons	580, 000		w e-
Deadweight, tons	500, 000	500, 000	400, 000
Shaft Horsepower		55-60,000	53,600
Speed, knots	18	17	15

The practical limits to tanker size are more likely to be geographic and economic rather than structural or fabrication limits. For example, representatives of Shell Oil Company have established 200, 000 dwt as an approximate practical limit, related to limiting European port drafts of 62 ft.

Speed increases have not followed the upward trend in size; in many cases the reverse has been true. Eighteen knot tankers such as the ESSO GETTYSBURG were operating in 1957, while the larger modern tankers are rarely designed to operate at sustained speeds above 16 1/2 to 17 knots. This is due largely to the fact that economics have dictated the installation of single screw machinery in the largest of the current tankers, with the exception of the MANHATTAN and the 276,000 dwt tankers under construction, and practical limitations have held the single screw power level to about 30,000 shp. Further, it is clear that the economics favor a relatively slow, full block hull form over a higher speed hull with less capacity.

Maneuverability, as illustrated by the tactical diameter, is also a significant factor in ship performance as it pertains to the ability to avoid collision. Table 3.1-4 gives some typical tactical diameters of representative tank vessels.

Arrangement Changes

「東京の東京の一大学校のからないできたからの一大学の大学の大学をはないないできませんできないできない。 かいしょう まんしゅう しゅうしゅう しゅうしゅう しゅうしゅう

Cargo Tank Length. The developments of most importance to the tanker operation have been in changes to cargo tank arrangement. The information in Table 3.1-2 shows that wing and center tanks of the postwar tankers were on the order of 40 ft in length, partly due to custom and partly due to regulatory body requirements. In the late 1950's, European tanker designs appeared in which alternate wing bulkheads were made nontight to serve as swash bulkheads, with the result that wing tanks were twice the length of center tanks. The American Bureau of Shipping soon relaxed its requirements and the first American flag tanker to be arranged in this manner was the SINCLAIR TEXAS, an adaptation of the conventional parent 46,000 dwt tankers developed by the Bethlehem Steel Company. The economies realized by this arrangement were the simple reduction in steel weight and the reduction in cargo piping, hatches, etc. resulting in a gain in cargo deadweight.

Vessel	CEDROS	N. News TKR"C"	N. News TKR"A"	ORIENTAL GIANT	ESSO SUEZ	NISSHO
LBP	940' 0"	685' 0''	535' 0"	804	900, 0.1	1906
Breadth	142' 0"	9310"	75' 0"	108	82' 6"	141
Depth	81, 0,,	48' 7"	40' 5"	i	42' 6"	72.9'
ш	54' 0"	36' 8"	31'9"	!	31, 10"	54.31
dwt	175,940	50, 200	25, 500	92, 980	34, 640	162, 300
dys	27, 500	26, 500	15,000	!	12, 500	28 000
W _K	18.3	19.5 5	18.8	17.6	16	. s.
Tactical Diameter, ft	3, 105	2,380	3. 200	2, 590	2 280	
Tactical Diameter, ft/LBP	3.31	3,47	5.97	3, 22) (1
Turning Circle, miles	1	† ;	1	2.34	: :	2.06

Cargo tank arra igement changes soon developed to the point where center and wing tanks were the same length, on the order of twice the earlier lengths. Regula try body requirements were established to limit the distance between swarp bulkheads to a maximum of $(\frac{LBP}{24} + 20)$ ft. Typically, then, mode tankers designed for minimum initial cost will be arranged with five tanabays, i.e., five cargo tanks in profile, with tank lengths about 2 $(\frac{LBP}{24} + 20)$ ft. For example, for a 700 ft ship, each tank will be approximately 98 ft long and will be fitted with an intermediate swash bulkhead, or an equivalent structure. This configuration is typical of the ships included in Table 3.1-3 and includes the recent American flag tankers ESSO HOUSTON and VALLEY FORGE, designed for service along the U.S. coast.

Other limits to length of individual cargo tanks have included informal requirements of the American regulatory bodies. U.S. flag vessels must maintain at least a one-compartment standard of damaged stability in order to qualify for a tanker load line assignment. It will be noted from Table 3.1-2 that some of the recent Japanese tankers are arranged with only four tanks in profile and probably cannot meet this standard under some conditions of loading.

Cargo Section Length. The proportion of cargo length to length between perpendiculars, has been increased significantly in the recent designs. This followed from the following observations:

- Hull bending moment due to cargo loading is reduced with increase in cargo length
- Increased cargo length, for constant overall dimensions and cargo deadweight, provides greater cubic capacity, with the resulting ability to load a full deadweight of lighter cargoes and/or the assignment of permanent clean ballast tanks
- Greater cubic capacity permits greater loading flexibility to obtain optimum trim and minimum stress.

Hull Arrangement Simplification. Consistent with the trend to greater cargo length was the elimination of forward fuel bunker spaces, particularly in the case of U.S. flag vessels operating over the relatively short coastwise runs, and the resulting elimination of the forward pumproom. This change permitted extending the cargo tanks forward. To

maintain ship trim, however, it was necessary to extend the cargo section aft by designing shorter machinery spaces. This was accomplished by elimination of the separation between engine room and boiler room and by compact rearrangements of machinery components and fuel bunkers.

Elimination of Amidship Bridge. This simplification, involving the location of all navigation and accommodation spaces aft, began with European tanker designs and was first adopted in the United States with the Bethlehem built SINCLAIR TEXAS. The advantages of this arrangement include reduced cost of house structure and crew outfit, simplification of controls and elimination of the catwalk between poop and bridge. Despite some early objections by pilots to this arrangement, the bridge aft configuration is in common use today on most new tankers, including ships over 100,000 dwt capacity.

Elimination of Superstructure. In this context, superstructure is defined as hull erections extending to the side shell, above the uppermost continuous deck. In the general trend toward simplification, some recent tankers have been built without either bridge or poop superstructure. In the limiting case, some recent Japanese tankers have been built as flush deck steamers. In this case, the tankers are assigned a steamer loadline, and accordingly, the ships are built with increased depth to obtain the required draft and displacement.

Accommodation and Navigation Spaces. Crew living standards have been greatly improved since the T2 standard in which crew members were berthed in three-man rooms and were provided with public toilet and shower spaces. Modern practice frequently includes provision of single-berth rooms for unlicensed as well as licensed crew, in fully air-conditioned quarters.

Navigation space visibility has been greatly improved, frequently by combining wheelhouse and chartroom into a single space, with 360° visibility. Advanced design bridges, resembling airport control towers, have been fitted on several large, European, bridge-aft tankers.

Hull Proportions

For a given deadweight requirement, minimum hull steel weight will be approached in the design process as length is reduced and breadth and depth are increased relative to a datum design. Proportions of recent tankers have tended toward reduced values of LBP/depth and LBP/breadth, as indicated in a comparison of these ratios in Tables 3.1-1 and 3.1-2. With increase in ship size, and generally no significant changes in operating speeds, designs have been produced with fuller hull forms, with few large tankers being built with block coefficients below 0.80.

Structural Design

Longitudinal Strength. Until fairly recently, longitudinal strength requirements were defined by the regulatory bodies as a minimum required section modulus, dependent on a relation of the following form:

$$I/y = f(L^2Bd)$$

where

L = length between perpendiculars

B = breadth

d = draft.

Later refinements to such relationship included consideration of the effects of cargo length variation and hull fullness.

Current rules of the major regulatory bodies require that the maximum still-water longitudinal bending moments be estimated by direct calculation for the range of expected loading conditions in order to obtain, rationally, a required section modulus. In some cases, it is also prudent, or required, to estimate the bending moments on a hogging or sagging wave to insure that realistic stress limits will not be exceeded. It is the practice of the shipyard to supply the classification agencies and the owner with a trim and stability booklet giving bending moment and stress information for the expected range of loading conditions.

Scantlings, General. Since the end of World War II, the various classification agencies have revised their scantling tables downward in accordance with extensive studies and tests of the various ship structural components. Accordingly, the weight of steel bulkheads, plating, etc. has been reduced significantly.

<u>Coatings</u>. The rapid corrosion of cargo tank structure, particularly for ships in the refined products trades, has been an occupational disease

of tank vessels in particular trades. The "Jumboizing" process saved the bow and stern of many tankers when it was necessary to scrap the wasted cargo section. In recent years, however, very effective epoxy and other tank coatings have been developed to protect against this source of deterioration. Accordingly, the classification societies, particularly the American Bureau of Shipping, have permitted the reduction in scantlings of selected areas of the cargo tanks by an amount equal to the corrosion margin, on the order of 1/16 in. plate thickness. This results in a steel weight saving, and a corresponding increase in cargo deadweight. on the order of several hundred tons, for tankers of 35,000 to 50,000 dwt capacity.

Castings and Weldments. Much of the end structure of ships, including the stern frame, rudder horn, stern shoe piece, etc., has traditionally been formed of large castings joined to the adjacent structure by Thermit welding or similar processes. Casting fractures have been common, particularly in the stern frame. To remedy these problems, weldments have been substituted and are universally used in some shipyards.

Rudder Design. The conventional double plate rudder with lower supporting shoe piece has largely been replaced, at least in American practice, by a horn type rudder, as originally designed for the MARINER class cargo ships. Even more recently, a full spade type rudder, eliminating all rudder horn castings, has been installed on the 36,000-dwt-American flag tanker VALLEY FORGE and will be installed on subsequent ships of the class.

Marine Engineering

From an inspection of Tables 3.1-1 and 3.1-2, it is clear that installed power has risen rapidly to the 30,000 shp level, from the 6,600 shp power level of the T2. The practical limitations lie in the amount of power that can be reasonably absorbed by a single screw propeller installation, on the order of 30,000 to 35,000 shp, rather than in the limitations of available prime movers. Steam-turbine machinery, chosen for 75% of the tonnage over 100,000 dwt, can be produced to supply any predictable power level needed for present and future tankers, while direct-reversing diesel engines, common in European practice, are available in powers approaching 30,000 shp. Economic limitations may dictate the installation of single

screw plants, at least up to the 300,000 dwt level. It should be noted, however, that the six, 276,000 dwt tankers under construction will be fitted with twin screw, steam-turbine machinery.

Steam conditions have also followed a steadily upward trend, from the 450 psi/740 $^{\circ}$ F conditions of the T2 to the standard 600 psi/850 $^{\circ}$ F plants of today. With modern reheat plants, as installed in the IDEMITSU MARU, steam conditions have advanced to about 1200 psi/950 $^{\circ}$ F.

The most recent development of interest, particularly in the U.S. coastwise tanker trade, is the simplification of machinery by the elimination of redundant equipment. In one design, for example, a single steam turbo-generator, a standby diesel generator set, and a minimum emergency diesel-generator set comprise the electric plant for a 15,000 shp steamturbine plant. This trend was carried further in the case of the ESSO HOUSTON, which is provided with a single main boiler.

Cargo Pumping

Cargo pumping systems are generally similar in arrangement to those of the postwar period, with the following exceptions:

- General elimination of the forward pumproom
- Increased pumping capacity. The 150,000 dwt TOKYO MARU, for example, can unload cargo in 24 hr.

Some basic changes have been accepted for particular trades, or in specific designs, including the following:

- Elimination of stripping systems--This simplification is possible with the adoption of some patented pumping systems or the use of self-priming pumps.
- Adoption of "Free-Flow" pumping systems--Where tank vessels are normally in single cargo trades, it is possible to replace the conventional piping system with a system of sluice valves installed in the tank bulkheads, and with simple suction and fill lines. By properly sequencing valve operations, cargo is pumped from the aftermost tank of a group. This system of cargo handling is characteristic of the French S.I.G.M.A. A.F.O. "Free-Flow" system.
- Installation of deep-well pumps--The conventional pump room may be eliminated entirely, as in the case of the ESSO HOUSTON, by

the adoption of vertical, deep-well pumps with the electric motor drive located on the weather deck.

Clean ballast systems -- Many of the recent tankers are designed to
operate with two or more cargo tanks assigned only to clean
ballast service. This arrangement results in reduced stresses
when in cargo service and provides useful clean ballast for the
ballast leg of the voyage. The ballast system is entirely independent
of the cargo oil system.

Deck Machinery

Provision of mooring winches and wire rope mooring is now accepted practice, and more advanced mooring systems involving use of universal chocks and constant tension winches are available. The latter are particularly useful for tanker service where rapid changes of draft occur during cargo loading and unloading.

Automation and Centralized Control

Pilot house control of main propulsion machinery, whether steam or diesel, as well as centralized control of all cargo pumping operations, are now state-of-the-art. In the latter case, one operator can maintain full control of all cargo handling operations.

Manning

Current U.S. Coast Guard manning requirements prescribe the following minimum manning standard for all cargo vessels, including tankers, with single-screw steam propulsion machinery:

Master	1
Radio Operator	1
Mates	3
Able-bodied Seamen	6
Ordinary Seamen	3_
Total, Deck Dept.	14
Chief Engineer	1
Assistant Engineers	3
Oilers	3
Firemen/Watertenders	_3_
Total Deck Dept.	10
Total Required	24

The rules make no requirements for mess department or other nonwatch standers. A realistic minimum requirement for a nonautomated, U.S. flag "austerity" tanker would include the following additional personnel:

Steward/Cook Cook/Baker Messmen	1 2
Total, Stewards Dept.	4
Pump Man Machinist	1 1
Total Utility Personnel	2
Total Complement	30

This is a realistic crew requirement for ships such as the ESSO HOUSTON or the VALLEY FORGE, which are in U.S. coastwise service.

Where centralized control and partial automation of the steam plant is provided, the U.S. Coast Guard permits the substitution of three "Deck-Engine Mechanics" for the required unlicensed engine department complement. The total complement is then 27 persons: the current complement on the ESSO HOUSTON.

The 30-man complement listed above is well below the crew size typical of the postwar fleet. The postwar ships typical of Table 3.1-1 carried crews as large as 50 to 73. It should be emphasized that reductions to as low as 30 men are possible, without automation, where labor union agreements permit and ship designs are simplified as in the case of the ESSO HOUSTON and VALLEY FORGE.

Safety

Upgrading of tanker safety standards, since the T2 tanker period, has been largely in the following areas:

Fire Extinguishing. Fixed deck foam systems are currently required for cargo protection in lieu of the previous steam smothering system.

Segregation. Quarters and other sources of ignition must be separated from cargo spaces by segregation spaces such as cofferdams, pumprooms, etc. Electric pump drives must be separated from cargo pumps by a bulkhead fitted with a gas-tight stuffing tube.

Materials. Special precautions are taken with respect to the striking of dissimilar metals in regions of cargo vapor. For example, use of certain aluminum anodes in cargo tanks has been diagnosed as a source of ignition.

Subdivision and Damaged Stability. Prior to the 1966 International Load Line Convention, tanker freeboard could be assigned without regard to the ability to withstand flooding damage. Informally, however, the U.S. Coast Guard has been imposing such requirements along with the trend toward larger cargo tanks. A requirement of the new Load Line Convention, however, is the ability to withstand the flooding of any compartment, within the cargo tank length, that is designed to be empty when the ship is loaded to the summer load waterline. For ships over 225 meters long, the machinery space is also to be tested as one of the empty compartments.

3.1.3 Hazards in Tanker Operations

The subject of pollution from collision and grounding, is well covered in the literature and is discussed in other sections of this report. However, other hazards to tank vessel operation should be considered as potential sources of pollution and are briefly discussed in this section.

Fire

Of the many possible disasters that may beset a tank vessel in petroleum trades, fire is probably the most common. Should rupture of a tank occur incidental to the fire, the cargo may be burned, thus preventing extensive pollution. It should be noted, however, that gross structural failures may occur as a consequence of fire damage, resulting in uncontrolled release of cargo that may not be consumed by the fire.

Explosion

Despite the many regulations and operational precautions, explosions occur when an obscure source of ignition takes place in the gaseous atmosphere above the liquid cargo level. Some of the most disastrous incidents have taken place when tankers in ballast, with empty tanks not gas-free, have been involved in minor collisions. A specific incident of unusual interest involved the use of certain aluminum cargo tank anodes that became

sources of ignition on impact with the steel structure. It is clear that disasters of this sort, while not necessarily involving collision or stranding, will result in gross structural failure and resulting release of oily ballast and cargo.

Structural Failure

The occurrence of major structural failures, hull fracture in longitudinal bending particularly, is well documented for ships built during the World War II period. Improper loading, notch sensitivity of steels, and poor structural details are all causes of failures. The potential release of cargo oil to the sea is a clear probability in these cases. Further, total fracture of the hull may separate part of the cargo section from the power source and pumping equipment.

3.1.3 Special Problems

Certain special types of marine liquid carriers have become relatively common since World War II and will continue to develop in the future. These are also potential sources of pollution and will be considered briefly in the following discussion.

Barges

The development of large, unmanned, seagoing barges is a relatively recent phenomenon, particularly in U.S. coastwise trade. Barges of 20,000 dwt capacity are in operation (4,000 tons greater than a T2 tanker), and serious proposals have been made for barges carrying over 30,000 dwt. The regulatory bodies have been aware of the potential hazards. It is clear that control problems in extreme weather and the succeeding events that could occur in event of collision or stranding, involving either the tug or barge, represent major pollution hazards. Certain automatic controls and safeguards have been provided: e.g., radio controlled release of the anchor and control of ballast pump operations and radio controlled steering in the case of certain conversions from ship to barge operations. In general, however, the ability to control release of cargo oil from a barge several thousand feet from the tug is limited, particularly in heavy weather.

Some promising developments have recently been publicized with respect to barge propulsion and operation. Of particular interest is the patented SEA LANK "push-tow" arrangement developed by Glosten. (130)

Similar developments are under study by Japanese and British designers and operators. These arrangements have the advantage of retaining the low investment and manning scale of the barge operation, while greatly improving performance, control, and maneuverability.

Special Cargoes

The design and construction of special product carriers as barges and self-propelled vessels, has evolved rapidly in recent years. With the great increase in such operations, this potential source of pollution should receive attention along with conventional tanker operations. Among the special cargoes being carried along the coasts of the United States are the following:

Molten sulphur Methanol Fertilizer solutions Hydrochloric and sulphuric acid Caustic soda Various petro-chemicals

Dry Bulk/Oil Carriers

Ships designed to carry either dry bulk cargoes, including coal, ore, etc., or liquid cargoes on alternate voyages have become increasingly common and are being built in sizes exceeding 100,000 dwt capacity. In certain configurations, where the cross section arrangement is similar to that of a high cubic, dry bulk carrier, a collision which would rupture the side shell would release an unusually large amount of cargo oil, since the usual tanker longitudinal bulkheads are absent. A recent design having this arrangement is described in Reference 132.

LITERATURE CITED CONCERNING DESIGN OF TANK VESSELS

TORREY CANYON Disaster

- 1. "TORREY CANYON: The Aftermath," Shipbuilding & Shipping Record. April 6, 1967.
- 2. "Marine Insurance Notes, re TORREY CANYON Disaster," Shipbuilding & Shipping Record, p. 501. April 6, 1967.
- 3. "Moves Following TORREY CANYON Affair," Shipbuilding & Shipping Record. April 13, 1967.
- 4. "A TITANIC Among Tankers," Shipbuilding & Shipping Record. May 11, 1967.
- 5. "IMCO Starts Problem Study," Shipbuilding & Shipping Record. May 25, 1967.
- 6. "Marine Insurance A Review of the First Half of 1967," Shipping World and Shipbuilder. July 20, 1967.
- 7. "The Safety of Tankers at Sea," Shipbuilding & Shipping Record. October 5, 1967.

Tanker Design

- 8. Specifications for the Construction of a Single Screw Tanker: Design T2-SE-A1: Turbo-Electric Propulsion, U. S. Maritime Commission. June 1941.
- 9. "Sun-Built T2-SE-A1 Tankers," Marine Engineering and Shipping Review. July 1947.
- 10. Robinson, Roeske, and Thaeler. "Modern Tankers," <u>Transactions</u>
 Soc ety of Naval Architects & Marine Engineers. 1948.
- 11. "Tanker OLYMPIC GAMES," Marine Engineering & Shipping Review.
 March 1949.
- 12. Brown, D. P. "Structural Design and Details of Longitudinally Framed Tankers," Transactions SNAME. 1949.
- 13. McDonald, J. H. and D. F. MacNaught. "Investigation of Cargo Distribution in Tank Vessels," <u>Transactions SNAME</u>. 1949.
- 14. "Bethlehem-Built Supertanker JAHRA," Marine Engineering and Shipping Review. November 1949.

- 15. deLuce and Budd. "The Design of a Class of 28,000 Ton Tankers," Transactions SNAME. 1950.
- Goldsmith, L. M. "Engineering of a 30,000 Ton Supertanker The First Ship Using 1020 Degrees F Steam," <u>Transactions ASME</u>, 1950.
- 17. Ireland, Wheeler, and Spencer. "The Performance and Design of Machinery for the 26,800 Ton Esso Supertankers," <u>Transactions SNAME</u>. 1951.
- 18. Pavlik, F. L. "30,000 dwt Tankers, Preview of a New Design," Philadelphia Section, SNAME. October 1951.
- 19. Bannerman. "A Structural Approach to the Problem of Corrosion in Tankers," <u>Transactions SNAME</u>. 1954.
- 20. Arnott. "Design and Construction of Steel Merchant Ship," published by SNAME. 1955.
- 21. Saunders. "Hydrodynamics in Ship Design," Vols. I, II & III, published by SNAME. 1957.
- 22. "Style Set by CITIES SERVICE BALTIMORE," Marine Engineering/Log. March 1957.
- 23. "ESSO GETTYSBURG Blue Ribbon Tanker," Marine Engineering/Log. August 1957.
- 24. Benford, H. B. "Engineering Economy in Tanker Design," Transactions SNAME. 1957.
- 25. "S. S. SANSINENA 60,000 DWT Supertanker," Marine Engineering/Log. March 1959.
- 26. Little, R. W. "Bibliography on the Longitudinal Strength of Ships and Related Subjects," <u>SNAME Hull Structure Committee publication</u> No. 2-3.
- 27. Earle, M. M. "The Conversion of T2 Tankers for Great Lakes & Seaway Service," <u>Transactions SNAME</u>. 1960.
- 28. Nichols, Rubin, and Danielson. "Some Aspects of Large Tanker Design," Transactions 2" ME. 1960.
- 29. Long, Stevens, and Tompkins. "Modern High Speed Tankers," Transactions SNAME. 1960.
- 30. "World's Largest Tanker Enters Service," The Shipping World. November 21, 1962.
- 31. Nakamura, Tsuneo. "Excellent Maneuverability of NISSHO MARU," Japan Shipping and Shipbuilding.

- 32. Katayama, I. "Maneuverability of NISSHO MARU," Japan Shipping and Shipbuilding.
- 33. Holly, H. H. "S. S. MANHATTAN, Largest Merchant Ship Ever Built in the U. S., " Marine Engineering/Log. April 1962.
- 34. "SINCLAIR TEXAS, U. S. Built Bridge-Aft Tanker Reduces Costs,"

 Marine Engineering/Log. August 1963.
- 35. "Some Examples of Synopses of the Reports of Scientific and Technical Studies on Large Tanker Building," Hitachi Shipbuilding & Engineering Co., Ltd., Technical Res. Lab., Osaka. August 1963.
- 36. "Largest Wear-Built Tanker Has Biggest O.K. Diesel," Shipping World. January 30, 1964.
- 37. "High Freeboard in Japanese Ships," Shipping World. February 6, 1964.
- 38. "Japanese Standard Tanker," Shipping World. March 19, 1964.
- 39. Sato, S. "The Design of 100,000 Ton dw Diesel-Engined Tankers," The Motor Ship. December 1964.
- 40. "The 99,655 Ton dw 27,600 dnp YAMAMIZU MARU," The Motor Ship, Supplement 29. December 1964.
- 41. "Meeting the Challenge of the Colonial Pipeline," Marine Engineering/Log. February 1965.
- 42. Johnson, R. P. and H. P. Rumble. "Weight, Cost and Design Characteristics of Tankers and Dry Cargo Ships," Maring Technology, vol. 2, no. 2. April 1965.
- 43. "A Massive Jumboizing Operation in Japan," Shipbuilding and Shipping Record. April 29, 1965.
- 44. "LAKE PALOURDE: Super to Maminoth," Marine Engineering/Log. August 1965.
- 45. Comstock. "Principles of Naval Architecture," published by SNAME. 1966.
- 46. American Bureau of Shipping Annual Report 1966,
- 47. Laskey, N. V. and G. T. R. Campbell. "The Design of Hull Forms for Supertankers and Bulk Carriers," vol. 3, no. 1, January 1966.
- 48. "TOKYO MARU, Size, Speed and Automation for Low Cost Transport of Crude Oil," Marine Engineering/Log. March 1966.
- 49. "Details of Large Tankers," European Shi ... Iding, no. 1. 1966.

- 50. "Some Design Considerations Regarding Large Tankers," <u>European</u> Shipbuilding, no. 2. 1966.
- 51. "ST. MIC1 ELIS First German Vessel Without Night Watch in Engine Room," Shipping World and Shipbuilder. June 1966.
- 52. "FORTUNA, New 'Duokleen' Tanker Construction," Shipping World & Shipbuilder. July 1966.
- 53. "SEA SPIRIT, Scandinavia's Largest Oil Tanker," Shipping World & Shipbuilder. August 1966.
- 54. Johnson, I. and B. Overbo. "Optimization Studies of Holl Construction," Part I, European Shipbuilding, no. 6, 1966, Part II, European Shipbuilding, no. 1, 1967.
- 55. Munro-Smith, R. "Applied Naval Architecture." 1967.
- 56. "The 500,000 Tondw Tanker ...," Shipbuilding & Shipping Record. January 5, 1967.
- 57. "Tankers of 500,000 dwt, Feasibility Study by Lloyd's Register of Shipping," Shipping World & Shipbuilder. January 19, 1967.
- 58. Kostell, G. "The Economics of Large Tankers," Shipbuilding & Shipping Record. Marc. 17, 1967.
- 59. "IDEMITSU MARU, Problems Associated with the Design and Construction of Mammoth Tankers," Shipbuilding & Shipping Record. April 13, 1967.
- 50. Tung, C. Y. "The Most Economical Tanker Size," Shipping World & Shipbuilder. June 1967.
- 61. Parker, T. J. "Approximate Hull Dimensions for 500,000 and 1,000,000 dwt Tankers," Shipping World and Shipbuilder. June 1967.
- 62. "SYMRA, Norwegian Shipyard's Largest Tanker," Shipping World & Shipbuilder. July 1967.
- 63. Swiss, M. "Limits of Tanker Deadweight Reached?," Shipping World & Shipbuilder, July 20, 1967.
- 64. "400,000 Ton dw Tanker," Shipbuilding & Shipping Record. July 27, 1967.
- 65. "Ships of 100,000 Tons dw and Over on Order," Shipbuilding and Shipping Record. September 1, 1967.
- 66. "Shell's Fleet of 200, 000-Tonners," Shipbuilding & Shipping Record. September 14, 1967.

Safety, Damage and Regulatory Bodies

- 67. Washburn, G. D. "Some Hazards Encountered in the Operation of Tank Vessels," Northern California Section SNAME. November 13, 1952.
- 68. Keeling and Stewart. "Use of Dry Flue Gas to Retard Internal Corrosion and Prevent Explosion in Clean Products Tankers," Transactions SNAME. 1953.
- 69. International Convention for Safety of Life at Sea 1960. SOLAS 1960.
- 70. Comstock and Robertson. "Survival of Collision Damage Versus the 1900 Convention on Safety of Life at Sea," <u>Transactions SNAME</u>. 1961.
- 71. Townsend, H. S. "Notes on Vessel Arrangement and Equipment as Related to Operating Procedure and Repetitive Damage," unpublished report of U. S. Salvage Association, Inc. December 1964.
- 72. Stanford, A. E. "What Inert Gas Systems Mean to "Marine Operator," Transactions SNAME. 1963.
- 73. "An Answer to Gas Hazards in Tankers," Marine Engineering/Log. July 1963.
- 74. Price, Cdr. R. I. "Coast Guard and '60 SOLAS," Proceedings of the Merchant Marine Council, U. S. Coast Guard. May 1965.
- 75. Reference deleted in final proofing.
- 76. Price, R. I. "The Implementation of SOLAS-1960," Marine Technology, vol. 2, no. 4. October 1965.
- 77. The International Convention of Load Lines. 1966.
- 78. Fletcher, A., Jr. "Tanker Damages," European Shipbuilding, no. 6, 1966.
- 79. "Safety at Sea," Supplement to Shipping World & Shipbuilder. June 1966.
- 80. Lancaster, J. H. "Safe By Design," Proceedings of the Merchant Marine Council, U. S. Coast Guard. August 1966.
- 81. "Aluminum Anodes & the U. S. Coast Guard," Petroleum Times. August 1964.
- 82. Bannerman, David B., Jr. "Highlights of the Load Line Conference, 1966," Marine Technology. July 1966.

- 83. Culver, C. A. "Progress in Marine Firefighting," Proceedings of the Merchant Marine Council, U. S. Coast Guard. November 1966.
- 84. Marine Engineering Regulations and Material Specifications, U. S. Coast Guard publication CG-115.
- 85. Goddu, L. W., Cdr. USCG. "IMCO, An Assistance to the American Merchant Marine," U. S. Naval Inst. Proceedings. December 1966.
- Load Line Regulations, U. S. Coast Guard publication CG-176, modified by Federal Register of 12/6/66 and 1/6/67.
- 87. "Carriage by Sea of Dangerous Substances in Bulk," unpublished report of U. S. Representative, IMCO Subcommittee on the Carriage of Dangerous Goods, 13th Session.
- 88. Rules for Building and Classing Steel Vessels, American Bureau of Shipping. 1967.
- 89. Rules & Regulations for Manning of Vessels, U. S. Coast Guard publication CG-268. May 1, 1967.
- 90. "Duokleen' Construction, an Added Safety Factor," Shipbuilding and Shipping Record. June 8, 1967.
- 91. "ALVA CAPE Explosion," Proceedings of the Merchant Marine Council, U. S. Coast Guard. June 1967.
- 92. Wade, C. S. "The 1966 Int'l Load Line Convention," Shipbuilding & Shipping Record. July 6, 1967.
- 93. Dilloway, Phillip. "Human Factors Affecting Merchant Ship Navigation Safety," Proceedings of the Merchant Marine Council, U. S. Coast Guard. September 1967.
- 94. Bonnebakker, J. W. "A Comment on Low and High Freeboard Tankers," Shipbuilding & Shipping Record. October 5, 1967.
- 95. Hayden, R. "Some Thoughts and Comments on Load Lines," Marine Technology, vol. 4, no. 4. October 1967.
- 96. Merchant Marine Council Public Hearing Agenda, USCG Publication CG-249. December 4, 1967 (proposed complete revision of CG-115, "Marine Engineering Regulations . . .").

Tanker Operation & Maintenance

- 97. Nichols, W. O. and C. E. Ericson. "Cargo Pumping Systems in Modern Tankers," Philadelphia Section SNAME. January 18, 1957.
- 98. Cowan, W. G. "Cargo Pumping Installations in Tankers," <u>Eastern Canadian Section SNAME</u>. March 11, 1958.
- 99. Shackelton, L. R. B., E. Douglas, and T. Walsh. "Pollution of the Sea by Oil," Transactions of the Inst. of Mar. Engrs., vol. 72. 1960.
- 100. "Remote Control for Handling Tanker Cargoes," The Shipping World. September 19, 1962.
- 101. Watson, P. "Automatic and Automated Cargo-Handling Aboard Tankers," Shipbuilding and Shipping Record, Int'l Design and Equipment Number. 1964.
- 102. Paterson, Ian. "Full-Rate Pumping for Final Stages of Cargo Discharge," <u>Tanker Times</u>. July 1964.
- 103. Hillman. "The Loading & Unloading of Tankers," Symposium on Ship Operation, Part 6, Transactions SNAME. 1955.
- 104. "Automation has Gone to Sea," Marine Engineering/Log. January 1965.
- 105. Purlee, E. Lee, W. A. Leyland, Jr., and W. E. McPherson.
 "Economic Analysis of Tank Coatings for Tankers in Clean Service,"
 Marine Technology, vol. 2, no. 4. October 1965.
- 106. Hays, Walter G. "The Service Rendered to the Shipping Industry by Marine Insurance and Some of the Problems Involved Therein," No. Cal. Section SNAME. 1966.
- 107. "Automatic Controls in Ships," Lloyd's Register of Shipping, 1966.
- 108. Higuchi, M. "Gravity Flow System for an Oil Tanker," J. Soc. Nav. Arch. Japan. June 1966 (in Japanese).
- 109. "The 'Vac-Strip' System Oil Tank Cargo Without the Use of Reciprocating Stripping Pumps," Shipping World & Shipbuilder. June 1966.
- 110. "A New Pumping Apparatus for Oil Clearance," HANSA, vol. 103, no. 14. July 1966 (in German).
- 111. "Automated Engineroom Control One Man Control in the DOLABELLA," Shipping World & Shipbuilder. October 1966.
- 112. "Oil on the Sea," Marine Systems. March/April 1967.

- 113. Symposium on Engineroom Automation Ship Operator's View, No. Cal. Section 5NAME. May 1967.
- 114. "Pollution How Operators are Keeping Clean," Marine Engineering/Log. June 1967.
- 115, Feck, A. W. and J. O. Sommerholder. "Cargo Pumping in Modern Tankers and Bulk Carriers," Marine Technology, vol. 4, no. 3. July 1967.

Maneuvering

- 116. Hewnis, E. F. and A. L. Ruiz. "Calculation of Stopping Ability of Ships," SNAME Ship's Machinery Committee, publication No. 3-4.
- 117. D'Arcangelo, A. M. "Guide to the Selection of Backing Power," SNAME, Ship's Machinery Committee, publication No. 3-5.
- 118. Pehrson and Mende. "Design, Model Testing and Application of Controllable Pitch Bow Thruster," N. Y. Metropolitan Section, SNAME. September 29, 1960.
- 119. Radford, Cdr. J. "Handling Very Large Tankers Problems Due to Weight and Length," The Shipping World. January 10, 1962.
- 120. Stuntz, G. R. and R. J. Taylor. "Some Aspects of Bow-Thruster Design," <u>Transactions SNAME</u>. 1964.
- 121. Hawkins, Seth. "The Selection of Maneuvering Devices," Chesapeake Section, Society of Naval Architects & Marine Engineers. September 20, 1965.
- 122. Wood, J. H. "Tankers and Bulk Carriers Will Need Kort Rudders," Shipping World & Shipbuilder. August 1966.
- 123. Schanz, F. "The Controllable Pitch Propeller as an Integral Part of the Ship's Propulsion System," <u>Transactions SNAME</u>. 1967.
- 124. Tothell, J. T. "Ships in Restricted Channels," Marine Technology, vol. 4, no. 2. April 1967.
- 125. "Test Results of Largest Bow Thrust Unit and Bulbous Bow," Shipbuilding & Shipping Record. September 21, 1967.

Related Marine Carriers

- 126. "Tank Sausages in Service," Tanker Times. September 1959.
- 127. Russo, Turner, and Wood. "Submarine Tankers," <u>Transactions</u> SNAME. 1960.

- 128. "Early Development of the DRACCNE Flexible Barge," 33rd Thomas L. Gray Lecture, Institute of Mechanical Engineers, January 25, 1961.
- 129. Foley, J. L. "Barges in Ocean Service," Transactions SNAME, 1965.
- 130. Glosten, L. R. and J. S. Heyrman. "Offshore Barge Transportation on the Pacific Coast," <u>Transactions SNAME</u>, 1965.
- 131. Dorman, W. J. "Combination Bulk Carriers," Marine Technology, vol. 3, no. 4. October 1966.
- 132. "CEDROS, Combination Oil/Bulk Cargo Carrier," Shipping World & Shipbuilder. January 1967.
- 133. "DRACONE Demonstrated at CAPRI," Shipbuilding & Shipping Record. February 2, 1967.
- 134. "ELRIDGE, First of a Sories of Three Combined Ore/Bulk/Oil Carriers . . .," Shipbuilding & Shipping Record. February 9, 1967.
- 135. Miller, C. D. "Economics of Superbarge Operation," Marine Technology, vol. 4, no. 3. July 1967.
- 136. Boylston, J. W. and W. A. Wood. "The Design of a Hinged Tanker," Marine Technology, vol. 4, no. 3. July 1967.
- 137. "SEA-LINK, Push-Tow Connecting Arrangement ...," Ship & Boat Builder International. September 1967.
- 138. "BALBINA, Japanese-Built Multi-purpose Carrier," S.W. and Shipbuilder. October 1967.

Special Products

- 139. Danielson, R. and H. McDonald. "The Design of the S. S. MARINE DOW-CHEM, Tankship for Special Commodities," New England Section, SNAME. September 1954.
- 140. "Sulphuric Acid Carrier CERES," Shipbuilding & Shipping Record. September 29, 1960.
- 141. Abrahamsen, E. "The Carriage of Special Liquid Cargoes," European Shipbuilding, no. 6, 1964, no. 1, 1965.
- 142. "The Sulphur Carrier LOUISIANA BRIMSTONE," Shipbuilding & Shipping Record. July 1965.
- 143. Engerrand, J. "About Safety Problems Involved in Certain Specialized Ships," <u>Bulletin Technique du Bureau Veritas</u>, Special English issue. <u>December 1966</u>.

114. Dyer, A. F., R. D. Goldbach, Cdr. R. I. Price, and R. J. Wheeler.
"Sending Chemicals to Sea," N. Y. Metropolitan Section, SNAME,
May 11, 1967.

Additional Bibliography

- 1. "Phase I Study Fairbanks Morse Advanced Diesel Motorship Machinery Plant, 20,000 SHP," Final MARAD Report, Contract N MA-3390, by M. Rosenbiatt & Son and Colt Industries.
- 2. Marshall, J. McC. "In the Black Wake of the TORREY CANYON," United States Naval Institute Proceedings. December 1967.
- 3. Hooft, J. P. and J. D. van Manen. "The Effect of Propeller Type on the Stopping Abilities of Large Ships," Shipping World & Shipbuilder. August 1967.
- 4. Tingey, R. H. "Tanker Design from the Operator's Viewpoint," Transactions SNAME. 1951.
- 5. Ireland, Wheeler, and Spencer. "The Performance and Design of Machinery for the 26,800-ton Esso Supertankers Built by the Newport News Shipbuilding and Dry Dock Company," <u>Transactions SNAME</u>, 1951.

3.2 OPERATIONS

When one considers the prevention of oil spillage, he must examine the various sources that potentially could release large quantities of persistent oil into bodies of water. These sources and their potential magnitudes and probabilities include the following:

SOURCE	MAGNITUDE	PROBABILITY
Oil Tankers and Other Ships	k Mare	
Overboard discharge	Moderate	Moderate
Collision	High	Low
Sanken tankers	Low rate	High
Offshore Production		
Inactive completions	Low	Low
Producing wells	High	Low
Drilling operations	High	Low
Pipelines	Moderate	Low
Undervater storage	High	Low
Natural Seepage	Low	Continuous
Industrial Waste	Moderate	Continuous

Moss⁽¹⁾ stated that there is general agreement that the most significant source of oil which pollutes the sea has its origin in ships; overboard discharge occurs following the cleaning of the cargo tanks of oil tankers and deballasting of tankers, dry cargo ships, and passenger ships. Oil tankers undoubtedly constitute the largest source of pollution due to ships because the tomage of petroleum moving by sea substantially exceeds the combined tomage of all other commodities.

Sufton stated that the discharge of tank washings is undoubtedly the biggest source of pollution and consequent fooling of beaches. (2) He goes on to conclude that in areas such as Northwest Europe where the beaches are polluted from time to time, the biggest source of pollution is from tankers which do not observe international convention, but clean tanks in prohibited waters.

The requirement for ballast in ships originates when they have partially or totally discharged their cargo and must proceed to another port. Sea water ballast must be substituted for cargo in order to maintain stability and seaworthiness both in transit and in berthing. (4) In the case of tankers on a ballast trip, the sea water might occupy as much as one third of the empty cargo tanks. (1) When the ship has berthed, the ballast water is pumped out prior to loading errgo, and because the ship is within port limits it is essential that the discharged water be clean. Therefore, in the past it has been the common practice by the tankers to wash down a sufficient number of tanks to provide vallast during berthing operations and to discharge overboard the oily residue from the washing.

The International Convention for the Prevention of Pollution of the Sea by Oil was drafted in 1954. The Convention, which came into force internationally in 1958, prohibited the discharge of persistent oil or oily mixtures in designated prohibited zones. (3) An "oily mixture" was defined as any mixture that contained more than 100 parts per million of persistent oil, and the prohibited zones were generally within 50 miles of any coast-line of the world excepting Eastern Canada, Australia, and Europe where the prohibited zones extended farther off the coastline. The Convention is insufficient because it unfortunately has not been ratified by all countries involved in the transportation of oil and furthermore permits any amount of persistent oil to be dumped outside of the prohibited zones; such oil could eventually reach coastlines. Further amendments were added to the Convention in 1962.

When the shortcomings of the Convention became apparent, industry instituted a program intended to eliminate a large percentage of the persistent oil pollution caused by deballasting and tank cleaning operations. The major oil companies do not presently discharge significant amounts of persistent oils at sea. (5-8) About 1964, the major companies instructed all of their vessels to immediately cease overboard discharge of any oily mixture exceeding 100 parts per million of persistent oil.

The residue that remains after tank washing procedures is pumped into one of the ship's normal cargo tanks designated a "slop" tank and allowed to settle until the oi' and water become separated. The separated water is then slowly decanted until mostly oil remain... This "slop" oil is

then either stored in special tanks at a terminal or retained aboard ship and combined with the next cargo in a procedure known as "Load-on-Top". The "Load-on-Top" $^{(1, 2, 3, 4, 6, 9)}$ procedure is estimated to be applied to about three-quarters of the crude oil tonnage moved by sea and is reported to avoid the discharge of as much as 1 1/2 million tons of oil annually. (3) Most refineries and a few repair yards have special facilities to receive "slop" oil. $^{(2, 13)}$

Oil-water separators have been tried at various times aboard ships and have not yet come into general usage. Prior to World War II, Maritime Commission C2 and C3 type ships were equipped with separators which gave unsatisfactory performance and therefore the requirement was relaxed. There have been attempts to use separators to produce a safe boiler fuel from tank-cleaning slop. Oil-water separators have also been designed and installed on dry-cargo and passenger ships. (12)

Some of the newer large tankers in use and under construction have separate tanks that are used exclusively for sea water ballast and completely eliminates the problem of oily residue when discharging ballast.

It is difficult to obtain statistics on the worldwide incidents involving collisions, strandings, or sinking of tankers. The Liverpool Underwriters Association indicates, for the period of June 1964 to April of 1967, that in 91 grounding incidents there were 17 cases of cargo spillage or leakage, and in 196 collisions involving 238 tankers there were 22 cases of spillage. Although Brockis concluded from these figures that the potential for oil pollution is greater for the case of collisions than for strandings, (3) a higher preentage of strandings result in cargo release. The probability of an oil spill due to a collision or stranding is much greater in the Gulf and East Coasts of the U.S. because of the larger volume of petroleum shipping as compared to the West Coast. (1)

In order to further reduce losses due to collisions or strandings, various training schools have been established for tanker personnel.

There are now special recommended routes issued by the major oil companies to their fleets for traffic through narrow and heavily travelled areas of the world where the danger of collision is the greatest. (7) The

U.S. government has also established "Shipping Safety Fairways" through the Gulf of Mexico areas of maximum offshore platform density. (14) These fairways will be shown on nautical charts.

Oil released from sunken tankers and other ships lying in waters off the U.S. coast is a constant potential source of pollution. There are 103 known sunken oil tankers off the U.S. coast. (15, 16) Moss stated that there were 61 tankers sunk off the U.S. coast by enemy action during World War II, containing over 5,000,000 barrels of crude petroleum and products. (1) These sunken tankers have consistently been blamed for oil s icks that suddenly appear along the coast to cause pollution. It is doubtful that these ships are significant sources of pollution.

Offshore oil wells are another potential source of a massive oil release. Even though the drilling operations and production wells are comprehensively covered by state and federal safety and antipollution regulations, there have been numerous accidents due to fires. storms, and collisions which have resulted in oil release. (17) Routine drilling and production operations on the offshore facilities generally do not create an oil pollution problem today due mostly to rigidly enforced state and federal antipollution laws. (18) Federal and state regulations covering oil well operations now require such safety features as blowout preventers, storm chokes, flame arrestors, fire-fighting equipment, and navigation warning devices such as lights and fog horns on drilling operations below certain depths and on producing wells. The various types of blowout prevention valves help keep oil spillage to a minimum in case of an accident. There are also comprehensive regulations covering usage of casings, such as depth required, size, and pretests. Abandoned wells must be plugged according to established regulations. (19)

In considering the possibility and potential magnitude of an oil release from an offshore platform, one must consider the number of wells in existence and the expected production for an average well. Currently, there are approximately 3000 active wells and 700 shut-in wells off the U.S. coast. (20) Calculations (19) have been made estimating the possible magnitude of release from an uncontrolled typical Gulf Coast offshore well. It was estimated that 79,000 barrels would be released over the six week period required to reestablish control. The upper limit expectation from

calculations by the same author based on the "Lakeview" gusher sets the volume of oil produced after six weeks at 2, 490, 000 barrels or about 3.7 times the TORREY CANTON cargo. It is pointed out that the probability of another "Lakeview" sized gusher is very small. No composite statistical records of number or magnitude of releases from offshore wells were identified in this study.

Underwater pipelines and storage tanks associated with offshore oil well production are designed, constructed, and tested to various safety codes. The oil transfer lines are buried a minimum of three feet under the sea floor and most contain sensing devices that stop the flow in the exact of a break in the line. Generally, due to economic considerations, oil is not currently stored underwater, but is either piped or shipped immediately to shore facilities. (19) However, some underwater storage tanks do exist on older drilling platforms with capacities as high as 20,000 barrels. (21)

Natural seepages exist off the coast of the U.S. mainly in two areas: the Gulf of Mexico and the Pacific Ocean off Southern California. These seepages, although a constant source of oil, do not present a major pollution problem. Moss points out two known natural seepages off the coast of Southern California and at least seven in the Carribean Sea. (1)

Refineries and other industries involved in processing oil with their respective unloading terminals on the shoreline generally cause very little pollution during routine operations. At most refinery unloading terminals equipment is available to prevent the spread of small spills (usually floating booms). Many terminals routinely surround the ship with a boom during any operation with potential for a spill. Some harbors have oil skimmers to remove small amounts of oil (see Section 4.7). Almost all ports have emergency equipment available to handle small spills, such as floating booms, straw, carbonized sand, and cement to absorb or sink the oil. (22)

<u>. .</u>

Literature Cited Concerning Operations

- Moss, J. E. "Character and Control of Sea Pollution by Oil," American Petroleum Institute. 1963.
- 2. Sutton, C.T. "The Problem of Preventing Pollution of the Sea by Oil," BP Magazine, vol. 14, pp. 8-12. Winter 1964.
- 3. Brockis, G. J. Preventing Oil Pollution of the Sea, Paper Presented at an Informal Meeting Biologische Anstalt, Helgoland. September 22-23, 1987.
- 4. Kirby, J. H. Pollution of the Sea, Paper Number 202 from the Conference La Petrole et la Mer, Monaco. 1964
- Ambrose, H. A. Oil Pollution of Seas, Coasts and Harbors, Gulf Research and Development Company Report no. 700R7001, September 1967.
- 6. Andreae, J. Standard Oil Company (New Jersey) and Humble Oil & Refining Company Testimony Regarding Senate Bills S. 1599 and S. 1604. June 7, 1967.
- 7. McEwan, H. "Esso Eliminates Pollution by Oil," Esso Marine News, 10(2), pp. 4-12. Summer 1964.
- 8. American Petroleum Institute. Oil Industry Action to Abate Pollution of the Seas by Oil Resulting from the Operation of Tankers. Statement released February 9, 1965.
- 9. Brummage, K. G., R. Maybourn, and M. F. Sawyer. "How LOT Affects Refinery Costs," Hydrocarbon Processing, 46(7), pp. 116-120. July 1967.
- 10.—Sait, P.—"The Deve pment of an Oil/Water Separator," Esso Marine News, 10(2), pp. 12-19. Summer 1964.
- 11. U.S. Department of State. Pollution of the Sea by Oil, Reply of the United States of America to questionaire on pollution of the sea by oil received from the Intergovernmental Maritime Consultative Organization. April 21, 1961.
- 12. Shackelton, L. R. B., E. Douglas, and T. Walsh. Pollution of the Sea by Oil, Paper Presented to The Institute of Marine Engineers, London. April 12, 1960.
- 13. "Keeping the Seas Clean," Esso Marine News, 10(3), p. 3. Winter 1964.
- 14. U.S. Department of Commerce. "Government Establishing Safety Traffic Lanes' for Shipping in Gulf of Mexico Oil Fields," News Release. November 14, 1965.
- 15. "Sunken Oil Tankers--'Time Bombs'," Clean Water Report. July 1967.

- 16. Fales, D. C. "Sunken Time Bombs Full of Oil," Popular Mechanics. p. 97. November 1967.
- 17. "CATC Tackles Big Well-Killing Job," Oil and Gas Journal, pp. 43-49. October 27, 1958.
- 18. "Oil Passes USGS Pollution Inspection Offshore," Oil and Gas Journal, p. 120. October 10, 1966.
- 19. NSIA Ocean Science Technology Advisory Committee, Special Study. July 10, 1967.
- 20. U.S. Department of the Interior. Petroleum Production, Drilling and Leasing on the Outer Continental Shelf. May 1966.
- 21. Lacy, R. and J. C. Estes. "Underwater Storage," Paper no. 123 from La Petrole et la Mer, Monaco. 1964.
- 22. Municipal Reference Library. Surface Pollution of Harbor Waters--Some Methods of Control, Milwaukee, Wisconsin. December 1966.

4.0 CONTROL OF O'L SPILLAGE

4.0 CONTROL OF OIL SPILLAGE

4.1 SURVEILLANCE AND PREDICTION OF SLICK MOVEMENT

4.1.1 Surveillance

One can readily appreciate the critical need for surveillance and prediction of slick movement of major oil spills. The rate and direction of movement of the slick as well as the extent of the affected area must be rapidly and effectively determined if appropriate action is to be taken to control the spill. In addition, surveillance is essential if the effectiveness of treatment methods is to be assessed. Aerial reconnaissance techniques appear to be the most practical for collecting the type of data needed to make judgments on the rates and direction of slick movements, control measures, and the effectiveness of control. These techniques offer greatest promise because large areas can be surveyed at near real time.

Aerial photography is probably the most economical surveillance tool that could be used to evaluate a major oil spill, although certain limitations are evident, such as weather conditions that may cause poor visibility and lighting and the fact that only daylight surveys are possible. Eliason (5) has pointed out that various types of film and filtering techniques may be used to enhance the contrast of oil-water surfaces.

Jamison⁽⁸⁾ also reports that the expensive and time consuming detection of pollutants in aquatic systems will be markedly aided by methods which can deal with extensive pollution-affected areas. He cites the considerable advantages of aerial photography.

Waldichuk⁽¹⁶⁾ reviewed the use of black and white film to trace surface currents by aerial photographic methods. Strandberg, ^(12, 13, 14) on the other hand, has used color film to make specific identifications of the nature and source of turbidity. He has also suggested that low levels of dissolved oxygen are detectable by this method. Oswald ⁽¹⁰⁾ supports this view, but implies that the detection of low levels of dissolved oxygen may be the result the bacterial activity associated with such environments. In reports of preliminary experiments, Carter ⁽³⁾ stated that freshwater vegetation probably loses its infrared reflectance upon death, and as a result, produces a white image on camouflage detection film. Camouflage detection film has been used extensively to detect unhealthy vegetation in agricultural and forestry applications. ⁽⁴⁾

Hom $^{(7)}$ and Fraga $^{(6)}$ have used aerial photography to conduct water pollution surveys directed toward evaluation of the biotic factors of the environment. In addition, Welch $^{(17)}$ and Kroeck $^{(9)}$ have applied similar techniques to water pollution control research.

Yost and Wenderoth (18) have devised a method for analyzing multiband negatives. Up to four negatives can be introduced into a multiple projection device that permits the superposition of the negatives on a screen and the addition of color. The result is an image of variable color composition which allows choices of proper color contrast for detection.

Ultraviolet and infrared imaging systems are available. (5) These systems collect surface radiation outside of the visible range and convert it into intensity modulated pictures in which the surface ultraviolet or infrared radiation intensity is converted to color or shades of gray. The Bendix Corporation of Ann Arbor, Michigan has developed and marketed an unclassified imaging system that is the first to be made available without military classification restrictions. The Bendix imaging system scans 60° either side of nadir and can be flown at speeds in excess of 200 miles per hr, which at 5000 ft above the surface allows an area of greater than 600 square miles per hr to be imaged. Eliason (5) stated that the data collected by imaging systems can be recorded on magnetic tape to be processed later by several techniques to bring out variations in radiation intensity levels that are often difficult to detect in the intensity modulated photo output.

The infrared imaging system is not limited to daylight surveys as are the photographic and ultraviolet systems. Although the infrared imaging system is not affected by smoke or haze, which limit photographic techniques, but it is limited by low clouds and fog. Depending upon the response of the microwave imaging system for oil-water surfaces, it might be very appropriate to use microwave techniques. (5) A microwave imaging system developed by Sperry Microwave Electronics Company of Clearwater, Florida for the U.S. Coast Guard may be capable of giving all-weather surveillance of large oil spills. (15)

The remote detection of pollutants in the environment using spectrophotometric methods has been proposed and developed to a limited extent by A. R. Barringer. (1) An instrument to detect SO_2 in the atmosphere has been developed, and an instrument to detect fish oil on the ocean surface is being developed to locate areas where fish are feeding. (2) Such a spectrophotometer could be employed in an aircraft for surveillance of oil slicks, but would be subject to cloud cover restrictions.

Dampening of surface waves by an oil slick may be detected by remote wave-height sensors used in aircraft. One such development underway at the U.S. Navai Oceanographic Office stems from initial research by the British National Institute of Oceanography in the early 1950's. (1) This concept, employing CW/FM radar, was pursued first in the United States by the Woods Hole Oceanographic Institution and subsequently by the U.S. Navai Occanographic Office and the Navai Research Laboratory. One system was designed to measure wave heights between 2 and 50 ft with an accuracy of 10% from an aircraft flying at 500 ft and at a speed of 180 knots. Such a system should be capable of oil slick detection regardless of cloud cover. Some problems in ambiguity of detection may result, and the effectiveness will be dependent on the spreading nature of the oil involved.

In summary, aerial reconnaissance of major oil spills offers greatest potential for surveillance and prediction of slick movement when radar, photographic, infrared, ultraviolet, and microwave imaging systems are employed. Microwave and radar imaging techniques appear to offer the best outlook for all-weather surveillance, particularly for large spills. Spectroscopic and photographic methods are more useful in low-level, thin film oil pollution situations. When meteorological data is added to this capability, accurate judgments should be possible. Since this field is relatively young, many research needs are evident.

Literature Cited Concerning Surveillance and Prediction of Slick Movement

- 1. Barringer, A. R. "The Possible Application of Remote C ochemistry in Planetary Exploration," Scientific Experiments for Manned Orbital Flight, vol. 4, AAS Science and Technology Series. 1966.
- 2. Barringer, A. R. "New Instrumentation to Meet the Pollution Problem." Proceedings of the Remote Sensing of Air and Water Pollution Conference, Sacramento, California, February 1967. Sponsored by Cartwright Aerial Surveys, Inc. 1967.
- 3. Carter, R. "Plankton Surveillance by Remote Sensing." Proceedings Third Annual Conference Remote Sensing of Air and Water Pollution. 1967.
- 4. Colwell, R. N. "Aerial Photography A Valuable Sensor for the Scientist," American Scientist, 52(1), pp. 16-49, 1964.
- 5. Eliason, J. R. Personal Communication, Pacific Northwest Laboratory, Battelle Memorial Institute, Richland, Washington, 1967.
- 6. Fraga, G. W. "An Experiment in Aerial Surveillance of Pollution Indices at Lake Tahoe," Proceedings Third Annual Conference Remote Sensing of Air and Water Pollution. 1967.
- 7. Hom, L. W. "Aerial Detection of Algae at Clear Lake and Lake Tahoe," Proceedings Third Annual Conference Remote Sensing of Air and Water Pollution. 1967.
- 8. Jamison, D. W. "Monitoring Water Quality with Aerial Photography," Annual Meeting Pacific Northwest Pollution Control Association, 1967.
- 9. Kroeck, R. M. "Non-Photographic Sensors," Proceedings Third Annual Conference Remote Sensing of Air and Water Pollution. 1967.
- 10. Oswald, W. J. "Remote Sensing Data and Evaluation of Water Quality," Proceedings Third Annual Conference Remote Sensing of Air and Water Pollution. 1967.
- 11. Schule, J. J. "An Airborne Wave Meter," Oceanography from Space, Woods Hale Oceanographic Institution. 1965.
- 12. Strandberg, C. H. "An Aerial Water Quality Reconnaissance System," Photogrammetric Engineering, pp. 46-54. Jamuary, 1964.
- 13. Strandberg, C. H. "Water Quality Analysis," Photogrammetric Engineering. March, 1966.

- 14. Strandberg, C. H. "Color Acrial Photography for Water Supply and Pollution Control Surveillance," Proceedings Third Annual Conference Remote Sensing of Air and Water Pollution. 1967.
- 15. Voss, Kurt. "Coast Guard Discovers that AN/AAR-33 Sperry Ice-berg Tracker Systems Aids Mapping." Technology Week. January, 1967.
- 16. Waldichuk, M. "Currents from Aerial Photography in Coastal Pollution Studies," Proceedings Third International Conference on Water Pollution Research, Munich. vol. 3, 1966.
- 17. Welch, R. I. "Remote Sensing Systems in Water Control Programs," Proceedings Third Annual Conference Remote Sensing of Air and Water Pollution. 1967.
- 18. Yost, E. F. and S. Wenderoth. "Multispectral Color Aerial Photography," Photogrammetric Engineering, 33(a), pp. 1020-1033. 1967.

4.1.2 Prediction of Oil Slick Behavior

The ability to predict the direction, rate of movement, and spreading of an oil slick in the event of a major release of oil is important in planning the deployment of defensive forces. This is important both in connection with actions to be taken immediately following a major oil release and based on real-time or short-range prediction of environmental conditions, and also in thorough contingency planning based on seasonal data.

Little information has been found in the literature directly discussing slick movement, although some fundamental knowledge is available which may be applied. Conversely more information applicable to the case of transport of dispersed oil is available particularly for specific areas. Example references are given (8, 13, 14, 18, 19, 24, 26, 28, 29, 30) relative to submerged transport of pollutants.

A number of citations (3, 6, 9, 10, 11, 12) provide historical data on surveys of coastal areas with discussion of the potential origin of the oil pollution.

The rate and direction of movement and spread of an oil slick from a point source is dependent on a number of variables. These include the following in estimated order of importance:

- 1. Wind direction and speed
- 2. Sea state
- 3. Surface currents
- 4. Latitude
- 5. Surface temperature
- 6. Oil density and viscosity at temperature
- 7. Volatility
- 8. Inherent tendency toward emulsification with sea water
- 9. Volume-rate of discharge at source
- 10. Interfacial and surface tension: spreading pressure.

All these variables are or can be time dependant.

Glude reported that Professor Denton of The Marine Biological Association Laboratory at Plymouth, England computed that a mixture

of oil and solvent is carried in the direction of the wind at a speed of 3 to 3 1/2% of the wind velocity. (16) This is in general agreement with experimental studies reported by Johnson on shallow wind drift currents. (21) These latter studies suggested drift rates on the order of 3 1/3 to 5% of the wind velocity. Height of wind velocity measurement was not given.

Johnson⁽²¹⁾ also pointed out that due to Coriolis forces, the wind drift at the surface is directed at 45° to the right of the wind in the northern hemisphere (to the left of the wind in the southern hemisphere) but may vary as much as 30 to 60°. The magnitude of this effect will be latitude dependant.

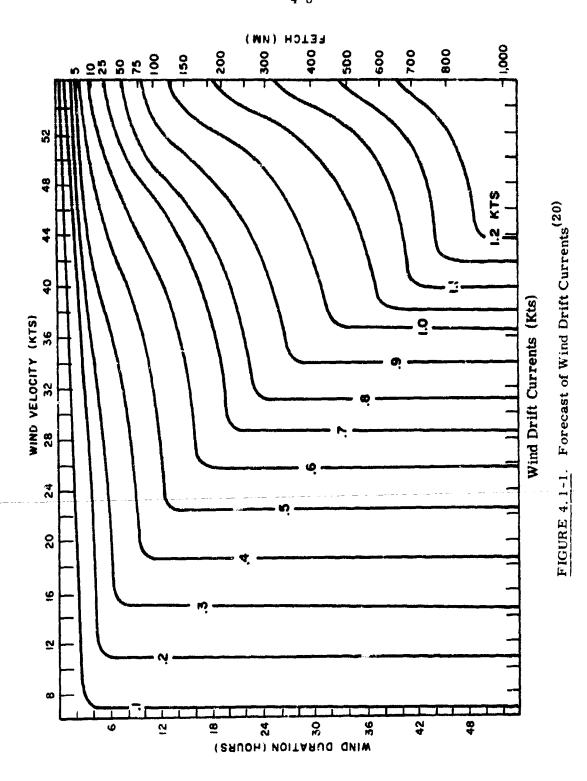
Phillips $^{(25)}$ and Hill $^{(17)}$ provided summaries of drag coefficients for the sea surface. These vary apparently linearly from approximately 5×10^{-4} to 2×10^{-3} over wind speeds from zero to 40 knots measured at a height of 10 m. Apparently then, the rate of drift of an oil slick might be expected to increase more than in direct proportion to increases in wind speed.

Cox and Munk (reported in Reference 17) provided a graphic indication of the effect of an oil slick on the mean-square-slope of the sea surface. The natural sea surface mean-square-slope increased linearly from 0 to 0.05 square radium over a wind speed from 0 to 15 m/sec, whereas an oil slick on the sea tended to hold the surface mean-square-slope constant at about 0.01 square radius up to a wind speed of 10 meters/sec.

James (20) provided a comprehensive and useful summary including calculation procedures for foreasting wind drift of surface waters. A comparison of observed and hindcast currents indicates good agreement. Figure 12 of James is reproduced here as Figure 4.1-1. This figure predicts somewhat lower values of drift rate: 2 to 3% of wind speed. James also suggests a 20° veering to the right (northern hemisphere) of wind direction as bein, "best estimate of the Coriolis effect.

In any event, the modification of wind drag coefficients by damping of water waves has not been considered in any of these correlations.

The properties of crude oil discharged to the sea surface change relatively rapidly with time due to the evaporation of the low boiling



BATTELLE NORTHWEST

fractions and to weathering. (23) Beynon, (4) for example, reported that samples of oil from the TORREY CANYON spill were consistent with Kuwait crude oil, with most of the material boiling below 300 °C removed. The material also represented a 30% water-in-oil emulsion, but went as high as 70% as time at sea continued. Smith (27) quoted Blokker (5) as indicating that ". . . 20% of Middle-East crude oil evaporated in about 11 hr, and 25% in about 40 hr" (temperature unspecified). Smith also pointed out that on March 24th following the TORREY CANYON stranding, the oil slick was 40 miles long and 10 miles wide. He stated further that, "Assuming that 30,000 tons of oil had come out of the wreck and was still all in this area, then the (average) thickness of oil would be 1 1/4 thousandths of an inch.

Blokker⁽⁵⁾ produces calculations for the spre d of crude oil on clean sea and suggests that . . . "about 1,000 tons would have spread out to a circle of 1,000 m in diameter in 90 min, that is, it would have covered about 1/3 square mile. In 10 hr it would be covering nearly 1 square mile. These figures correspond quite reasonably with the sort of spread of the larger quantities of oil from the TORREY CANYON."

The American Petroleum Institute (reported in Reference 1) investigated the spreading of oil on water surfaces and presented the following tabulations of thicknesses and description.

Gallons of Oil Per Square Mile of Surface	Approximate Film Thickness, In.	Appearance
25	1.5 x 10 ⁻⁶	Barely visible under most favorable light conditions
50	3.0 x 10 ⁻⁶	Visible as a silvery sheen on surface of water
100	6.0 x 10 ⁻⁶	First trace of color may be observed
200	12.0 x 10 ⁻⁶	Bright bands of color are visible
666	40.0×10^{-6}	Colors begin to turn dull
1332	80.0×10^{-6}	Colors are much darker

Films up to 3.0×10^{-6} in. do not persist for more than five hours on agitated water surfaces. A slug of oil at sea required 40 to 100 hr to thin out to 40×10^{-6} in. but thereafter disappeared entirely in less than 24 hr. The API reports that oil may be discharged uniformly at a rate of 10 gal. per hr per square mile without becoming visible, but a rate of 28 gal. per hr per square mile would result in a continuous iridescent film.

Dennis (11) in discussing oil pollution surveys of the Southeast Florida Coast developed an excellent correlation between seasonally prevailing wind direction and the quantity of oil stranded on the beaches. He also provides some discussion of current effects in that area. Dennis (9) provided similar information for the Southeastern New England Coast.

Galvin and Nelson⁽¹⁵⁾ provided a compilation of published longshore current data available from North American sources as of January 1966 including 127 observations from field studies. Although this work was directed primarily toward prediction of littoral transport rates, it may have value in prediction of near-shore transport of oil slicks and dispersions.

Literature Cited Concerning Prediction of Slick Movement

- 1. Anonymous. "Deposit of Refuse in Navigable Waters Generally," Code of Federal Regulations Title 33-406.
- 2. Anonymous. "Oil Pollution Research," Engineer, vol. 196, p. 556, 1953.
- 3. Anonymous. "Tanker Survey of the Gulf Stream Key West to Cape Hatteras," Oil Pollution Panel of Merchant Marine Council, United States Coast Guard. November 6, 1956.
- 4. Beynon, L. R. "The TORREY CANYON Incident," British Petroleum Company Limited, September 1967.
- 5. Blokker, P. C. "Spreading and Evaporation of Petroleum Products on Water," 4th International Harbour Conference Antwerp, Belgium. June 1964.
- 6. Determination of the Quantity of Oily Substances on Beaches and in Nearshore Waters, California State Water Pollution Control Board, Publication no. 21, part 1, 1959.
- 7. Characterization of Coastal Oil Pollution by Submarine Seeps.

 California State Water Pollution Control Board. Publication no. 21,
 part 2. 1959. Proceedings of the First International Conference
 on Waste Disposal in the Marine Environment, July 22-25, 1959,
 Pergamon. 1960.
- 8. Carter, H. H. and A. Okubo. "A Study of the Physical Processes of Movement and Dispersion in the Cape Kennedy Area." U.S. AEC Report NYO-2973.
- 9. Dennis, J. V. "The Relationship of Ocean Currents to Oil Pollution off the Southeastern Coast of New England," Amer. Petrol. Inst. January 23, 1961.
- Dennis, J. V. "Oil Pollution Conditions of the Florida East Coast," Amer. Petrol. Inst. March 15, 1960.
- 11. Dennis, J. V. "Oil Pollution Survey of the United States Atlantic Coast with Special Reference to Southeast Florida Coast Conditions," Amer. Petrol. Inst. May 15, 1959.
- 12. Dennis, J. V. "Oil Pollution Survey of the Great Lakes within United States Territorial Limits," Amer. Petrol. Inst. January 15, 1960.
- 13. Fisher, L. J. Personnel Communication, U.S. Naval Oceanographic Office. August 11, 1967.

- 14. Foxworth, J. E., R. B. Tibby, and G. M. Barsom. "Dispersion of a Surface Waste Field in the Sea," Journal Water Foll. Con. Fed., vol. 38, no. 7, pp. 1170-93. 1966.
- Galvin, C. J. and R. A. Nelson. "Compilation of Longshore Current Data," U.S. Army Coastal Engineering Research Center Miscellaneous Paper No. 2-67. March 1967.
- 16. Glude, J. B. and J. A. Peters. "Recommendations for Handling Oil Spills Similar to that from the Tanker TORREY CANYON." Unpublished Report. June 1967.
- 17. Hill, M. N. The Sea, Vol. I, Physical Oceanography, Interscience Publishers, pp. 57-87. 1966.
- Holley, E. R. and D. R. F. Harleman. "Dispersion of Pollutants in Estuary-type Flows," M.I.T. Hydrodynamics Laboratory Rept. No. 74. Water Poll. Abs. (Brit.), vol. 38, p. 1633. 1965.
- 19. Ingram, W. T. and H. Mitwally. "Paths of Pollution in New York Harbor: A Model Study," <u>Journal Water Poll. Cont. Fed.</u>, 38(10), pp. 1563-1581. 1966.
- 20. James, R. W. "Ocean Thermal Structure Forecasting," ASWEPS Manual, vol 5, U.S. Naval Oceanographic Office Report SP-105.
- 21. Johnson, J. W. "The Encyclopedia of Oceanography," R. W. Fairbridge, Editor, The Reinhold Publishing Corp., New York, pp. 587-590. 1966.
- 22. Langmuir, I. "Surface Motion of Water Induced by Wind,"
 Science, vol. 87, pp. 2250, 1938.
- 23. Moss, J. E. "Character and Control of Sea Pollution by Oil," Amer. Petrol. Inst. October 1963.
- 24. Niles, T. M. "Dispersal of Pollution by Tidal Movements,"

 Jour. San. Eng. Div., Proc. Amer. Soc. Civil Engr., vol. 83(5),
 p. 1408. 1957.

. .

- 25. Phillips, O. M. The Dynamics of the Upper Ocean, Cambridge University Press, 1966.
- 26. Pyatt, E. E. "On Determining Pollutant Distribution in Tidal Esturaries, Hydrology of Tidal Streams," Geological Survey Water-Supply Paper 1586-F.
- 27. Smith, J. W. "The TORREY CANYON Disaster," Paper given to the Annual Meeting of the British Association for the Advancement of Science, Leeds, England. September 6, 1967.

- 28. Thomann, R. V. "Recent Results from a Mathematical Model of Water Pollution in the Delaware Estuary," <u>Water Resources Res.</u>, vol. 1, p. 349, 1965.
- 29. Waldichuk, M. "Currents from Aerial Photography in Coastal Pollution Studies," <u>Journal Water Poll. Cont. Fed.</u>, 38(3), pp. 394-395. 1966.
- 30. Welsh, J. G. "A New Method of Measuring Coastal Surface Currents with Markers and Dyes Dropped from an Aircraft," J. Marine Research 25(2), p. 190. 1967.

4.2 CHEMICAL TREATMENT--COLLECTION AND SINKING

The TORREY CANYON incident brought to light numerous materials which offer potential for removing oil slicks from the surface of the sea by facilitating either the collection or sinking of the oil. The function of these materials is to preferentially cause the adherence of oil to some surface while excluding sea water. The resultant mass then either sinks to the bottom of the sea or is physically removed from the surface for processing or disposal.

The literature shows that the following materials have been employed in actual field situations or in the laboratory with varying degrees of success:

Collection Agents

Absorbents

Straw
Sawdust
Rope
Bark
"Ekoperl"
Chrome leather
Polyurethane foam
Polypropylene fiber
Copolymer PVC/PVA

Cotton waste

Absorbent felt paper

Waste paper

Peat

Rock wool sheets

Glass wool Rayon floss Sisal string

Congealing Agents

Plastic foam Plastic film Nylon agglutinants

Gelling Agents

Molten wax Soaps

Demulsifying Agents

(unspecified)

Sinking Agents

Sand
Brickdust
Fly ash
Cement
China clay
"Omya" clay
Volcanic ash
Silicone mixtures
Carbonized sand
Vermiculite
Crushed stone
Slaked lime
"Stucco"

Collection Agents

One of the oldest techniques for dealing with oil spills is to spread straw on the water. (8, 14) Straw is a very good oil absorbent; in fact, it was reported to have worked extremely well in the TORREY CANYON incident although high winds proved to be a problem in laying down the straw. Beynon reports that another problem in the use of straw--or, for that matter, any other absorbent--is in its collection. He states that the collection problems can be enormously reduced by towing booms or nets containing the straw toward sheltered areas near shore, where collection is markedly easier. An added advantage of straw is that the oil-straw mass may be easily disposed of by burning.

In an attempt to combine several of the previous suggestions, booms made of straw have been used. (1) Several reports point out that the collection of the straw can be facilitated if some type of aggregating or gelling material is added. (3, 5) The straw mass can be collected far easier if treated in this manner.

Sawdust, also a long-used method for absorbing oil spillage, was poured on oil patches by the French during the TORREY CANYON incident. (8) The sawdust was distributed by French naval vessels and then scooped up by accompanying ships trailing behind. The method was used successfully around the LeHavre port area. The French now believe that, if the sawdust had been impregnated with a detergent, results would have been even more successful. Ambrose (19) points out that sawdusi, like straw, can be burned after collection. He suggests that burial might also be appropriate. Glude (23) states that oil sawdust mixtures were very difficult to handle on shore. Sawdust tended to plug equipment used to pump the mixture into containers or from containers to a disposal plant in Brest.

Rope also will absorb oil; (1) however, this observation usually was made in conjunction with the fact that rope was widely employed to hold together booms of other absorbent materials such as straw.

Kornaes-Marma AB, a Swedish forest products company, has utilized powdered bark successfully to absorb floating oil. Clumps of bark-oil mixture form, and these can be collected and burned. (16)

Caldwell (21) notes that an oil absorbent material called "Ekoperl" has been demonstrated at the Laboratoire Central d'Hydraulique in Paris. It appears to be similar to another material. Perlite. (44) Caldwell described this German-made material as being a cotton-like substance. However, Ambrose (19) reports that "Ekoperl" is said to be a porous, dried volcanic glass containing aluminum silicate, and is chemically treated to repel water and absorb oil. Ambrose further reports that 70 cubic feet of "Ekoperi" absorbs one ton of oil. The cost of "Ekoperl" was given as about \$70 (U.S.) per cubic meter (\$2 per cubic foot or \$140 per ton of oil). Caldwell (21) reports that in a demonstration, motor oil was dispersed in a large beaker by vigorous stirring followed by addition of "Ekoperl". There was immediate selective absorption of oil from the water. Later in the year, when a Greek tanker discharged oil threatening the Swedish Gothenberg Archipelago and Harbor, "Ekoperl" was used on the oil causing it to lump together. Straw was then spread on the agglomerated mass to assist in collection. The method proved to be highly successful, and damage to beach sites in the area was minor.

Scientists at the United Kingdom Atomic Energy Authority facility at Harwell recommended the spreading of tanner's waste (leather shavings treated with chromium salts) on the TORREY CANYON oil slick. (8) The shavings are said to reject water and absorb oil. (4) It was anticipated that when the oil was absorbed the shavings would be collected and burned. This was tried, but it proved to be ineffective. (8)

A shredded polyurethane foam has been developed by J. Bibby and Sons of Liverpool, England, for Esso Petroleum of Great Britain. The polyurethane has a marked ability to soak up oil. A demonstration by Esso Petroleum in which the polyurethane was spread onto the oil slick and then towed ashore was reported to be highly successful. Roughly 50 cubic feet of foam will soak up about a ton of crude oil. The oil can be pressed out of the foam for reuse. About 80% of the absorbed oil can be recovered by pressing. The cost of this technique is \$13 per ton of foam plus application and collection costs. Use on residual or other highly viscous oils has apparently not been demonstrated, however related work in Japan (26) indicates more viscous oils may be more effectively absorbed.

National Textile Research Institute of Japan has initiated a project to develop a polypropylene fiber in which styrene is graft-polymerized under gamma irradiation. The group has completed preliminary studies on a beaker scale and, as the next stage, will carry out water pond studies. If such a fabric is made into a huge net, it could prevent spreading of an oil slick. (10)

Related studies were conducted at the Warren Spring Laboratory prior to 1963 with a copolymer, e.g., PVC/PVA. As far as is known, no further work was done and the method was not employed at the time of the TORREY CANYON disaster probably due to the high costs of this technique.

Both Ambrose (19) and Beynon (20) report that the French used plastic foam as a congealing or absorptive material. The plastic was used on patches of oil off the coast of Brittany. The oil collected can be recovered from the plastic foam. The type of foam was not specified. It is possible that the plastic material used was that developed in British Patent 979,978. (22) The patent claims that a flexible plastic film can be formed on the surface of an oil slick by spraying the plastic in a solution of a volatile solvent such as acetone. The film may be formed as a continuous sheet, or as a web of thread-like filaments which penetrate beneath the surface of the oil. Gall states that the film can be effectively applied by spreading from aircraft.

Glude (23) reports that the French employed "nylon and plastic agglutinants." Although expensive, these substances made removal of the oil from beaches easier and facilitated burning.

Several compounds have been used to convert oil slicks into gel-like solids which can be collected from the water surface for subsequent disposal. Humble Oil Company⁽¹²⁾ reportedly is developing such gelling compounds. The Yosemite Chemical Company already markets such a gelling compound under the trade name "Spillaway" for the specific purpose of controlling oil spills. Patents indicate that oil can be congealed by spraying with molten wax, liquid metal soaps of wool grease acids, or divalent metal soaps of wool grease fatty acids with nonionic surface active agents in a petroleum diluent. (48, 49)

Demulsifiers are commonly used in shipboard systems to break emulsions in ballast water so that wastewater cleanup can be effected. Two documents by the Petrolite Corporation describe such systems.

Demulsifiers are generally proprietary and are usually compounded by Edisonian techniques to meet field conditions at the use site.

In summary, collection agents generally fall into four categories: absorbing, congealing, gelling, and demulsifying agents. Their function is to cause the oil either to adhere to a solid surface or to react chemically with another liquid, thus forming a collectable mass. The selection of the type of collecting agent is based upon the desired objectives of the cleanup program, e.g., efficient oil recovery for reuse, combustion of recovered residues, or economical and rapid action.

Sinking Agents

Work on sinking of oil at the Warren Spring Laboratory⁽¹¹⁾ prior to 1963 is summarized in the following quotations:

"An apparently promising method for the treatment of floating oil is the distribution over the oil patch of a powder or fine granular solid of high true density which admixes with the oil, adheres to it and sinks it. An essential requirement is that the solid material should so fix and retain the oil that once submerged no oil is released to renew the contamination. Ideally the submerged mixture of oil and powder should set to a solid mass so that the oil is completely immobilized. A number of proprietary materials are marketed which, it is claimed, fulfill all the necessary requirements. A full investigation of one of these was undertaken but it was considered to be unsatisfactory because of its inability to retain permanently the sunken oil. After several months under water the sunken mass was still mobile and oil could be released from it by agitation.

"Other, more common and cheaper materials such as sand, brickdust, crushed clinker and Portland cement have been found to be equally effective for sinking oil but no material examined to date has possessed adequate oil retention properties. If the oil could be treated with a sufficiently large

quantity of some of these powders it might be permanently immobilized, but in practice, before this can be accomplished the oil becomes heavier than water and sinks, carrying with it an insufficient quantity of powder to render it immobile. Furthermore, the practical difficulty of spraying or otherwise distributing powdered solids in the open air to give sufficient and uniform coverage of the oil has not been overcome. Distribution by helicoper has been considered but not attempted.

"It is understood that the fishing industry would object to the use of this method as the mobile, sunken oil is liable to foul fishing gear; sinking of oil would have to be avoided in the vicinity of beds of oysters or other shellfish.

"This method is not recommended."

In another Warren Spring Laboratory report, (29) the weight of sand required is reported to be 110% of the weight of oil in laboratory tests. Under field conditions this amount will probably be totally inadequate. Refloating of the oil was also noted with untreated sand although carburized sand was apparently permanently effective at least in laboratory tests. The practical logistics and distribution problems associated with a large slick at sea were also noted.

Immediately after the TORREY CANYON disaster, the British carried out tests at sea with china clay in an effort to sink the oil. (4) Although the tests appeared to be successful, authorities decided that, in the waters off southwest England, there might be some danger to the fishing grounds. There was also some doubt if such an agent would actually be able to prevent the oil from resurfacing. (8)

In an attempt to sink the oil at sea beyond the continental shelf, the French applied large quantities of agglomerating agents, such as volcanic ash or the clay "Omya". (23) This method appeared to be of considerable value and it was felt that the total volume of oil had been reduced substantially by the application of finely powdered clay at sea. This flocculating technique is less effective after oil is smulsified by application of detergents.

The application of Omya is very expensive as it is reported to cost 120 francs (\$24) per ton. (24) Roughly two pounds of clay would be needed to sink a gallon of oil weighing seven pounds. On this basis, 34,000 tons of Omya costing over \$800,000 would be required to sink all of the oil from the TORREY CANYON. In addition, there would be the cost of applying the clay at sea.

Pleuss-Staufer (North America) $^{(28)}$ manufactures a material called OMYA-BH which appears to be powdered $CaCO_3$, with a coating of about 1% stearic acid. The acid gives the powder its hydrophobic quality. Relationship of this material to that reported by Glude is not known.

The French found coal cinders were another successful absorbent. (8) Since this is a waste product from the utility industry, use was quite economical. In addition, the cinders proved to be lighter than sawdust. Beynon (20) also cites the use of ash as an absorbent in the TORREY CANYON cleanup.

A new method of absorption using fly ash has been reported. (2)

Joint testing by the Central Electricity Generating Board and Midland Silicones

Ltd. in Britain showed that pulverized fly ash treated with silicone will sink

crude oil. When treated with silicone, pulverized fly ash becomes hydrophobic but absorbs oil and then sinks. In possibly related work, Cardiff

University has devised a scheme using fly ash, coated by gaseous silicone
treatment, for use in a weight ratio of about 2 to 1 ash to oil. (13)

Reference has also been made to the use of carbonized sand as an absorbent. (5) When carbonized sand is spread on the oil surface, the oil agglomerates and the resultant sand-oil mass sinks. According to Lovell, (27) ..., carbonized sand does not appear to be a very effective means of removing large spills (thick oil layers) but has been reported to be effective in cleaning up thin films of oil in relatively quiescent water. A description of this product and pictures appeared in Life magazine 10 November, 1947. Carbonized sand was employed by the USS SHANGRI-LA following release of a quantity of fuel oil off Cannes, France, in 1965. Pilpel (32) and Standard Oil of California (33) also report the use of carbonized sand. Both Monsanto Chemical Company and Dynasurf Chemical Corporation manufacture a treated sand which absorbs oil and then sinks. (34)

The French used fine natural sand for much the same purpose. (19)
Beynon reports that the mineral, vermiculite, has also been used as an absorbent spread on the surface of the sea. Stone, ground finely and spread on an oil slick, has been successful in sinking oil. (1)

After measures had been implemented by the British to sink oil spilled by the TORREY CANYON, authorities concluded that, based on field results, a combination of sinking agents, silicones, and oil metabolizing bacteria might be a suitable method for preventing the resurfacing of sunken oil. (8) This method was not attempted because at the time of the TORREY CANYON incident, sufficient stocks of material were not available.

The Danish government has developed a new powder, the composition of which is not specified, which absorbs and sinks oil. (19) The reported cost of the powder was \$0.01 per pound. The powder reportedly absorbs an equal weight of oil. Another reference (18) reports that the Danish Oil Destruction Company has developed a 95 to 98% sand product which absorbs oil in the ratio of 3 to 1 (sand to oil). They claim that oil is firmly held, not rising to the surface if operating instructions are followed. Whether this is the same product mentioned in the previous reference is not known.

Slaked lime (25) and "stucco," (11) a residue from phosphoric acid manufacture, have both been used to absorb oil and then sink. Herbinger (30) reports that barium sulfate iron ores, and aluminum and magnesium silicates, calcium and magnesium carbonates etc. have an affinity for hydrocarbons that can be increased by addition of 0.05 to 1% by weight of surface active agents. Added to contaminated waters, they induce sedimentation of hydrocarbons and promote biodegradation.

Sturz and Klein⁽³¹⁾ report on the testing of binding media for removal of oily impurities in surface waters. A list of patents on absorbent and sinking materials is appended (References 35 through 55).

In summary, numerous sinking agents are available for dealing with oil spills although no quantitative comparative data on their effectiveness were found in the course of this study. Several substantial problems with the use of sink agents are evident. First, logistics of supply and dispersal of the agent is difficult, particularly in the case of large spills. Second, the sunken oil may have substantial adverse effects on demersal fish species. Third, resurfacing also poses a considerable problem. Fourth, application is more efficient with relatively thin oil films.

As a result, the use of sinking agents is recommended only in deep water beyond normal fishing ground, i.e., off the continental slope. Resurfacing of the oil will probably occur, but it will be gradual and the oil washing ashore will generally be well weathered and less objectionable.

Literature Cited Concerning Chemical Treatment -- Collection and Sinking

- 1. Anonymous. "Britain Arrested TORREY CANYON'S Sister Ship," Chemical Engineering. July 31, 1967.
- 2. Anonymous. "Flexible 'Dracone' Picks up Oil Slicks" and "Flyash Serves for Oil Spill Cleanup," Air & Water News, vol. 1, no. 18. May 8, 1967.
- 3. Anonymous. "Greek Tanker Drops Oil on Swedish Shores," Air & Water News, no. 19. July 17, 1967.
- 4. Anonymous. "Oil Products: It's Easier to Keep Them Aboard Than to Tay to Pick Them Up," Air and Water News. 1(14). April 3, 1967.
- 5. Anonymous. "Pollution by Oil is a Much Tougher Problem for Ships," Marine Engineering/Log LXXII, no. 6, p. 39. June, 1967.
- 6. Anonymous. "Shredded Polyurethane Absorbs Oil Spilled on Oceans," Chem. & Eng. News. September 25, 1967.
- 7. Anonymous. "Technology. Mopping Up Oily Oceans," Time, vol. 90, no. 4, p. 68. July, 1967.
- 8. Anonymous. "TORREY CANYON Spill Proves Good Testing Ground for Oil Clean-up Techniques," Air and Water News. March 15, 1967.
- 9. Anonymous. Norfolk Navy Yard Report 262551. February 19, 1952. Also U. S. Patent 2, 464, 204.
- 10. Anonymous. Air and Water News, p. 5. October 2, 1967.
- 11. Anonymous. "The Treatment and Disposal of Floating Oil," Warren Spring Laboratory, Ministry of Technology United Kingdom, Report No. RR/ES/40. April 1963.
- 12. Anonymous. "The Treatment of Oil Pollution," <u>The Baltimore Sun,</u> October 13, 1967.
- 13. Anonymous. "Chemicals vs. Crude Oil," Chemical Week. May 5, 1967.
- 14. Anonymous. "Test of Straw as an Absorbent," International Oceanographic Foundation, p. 5. September 1967.
- 15. Anonymous. "Fuel-Ash-Silicone Absorbent," Cardiff University, Science News, p. 343. October 1967.
- 16. Anonymous. "Powder Made from Tree Bark Effective in Fighting Oil Spills," Chem. Eng., p. 80. October 23, 1967.

Face of the second seco

- 17. Anonymous. "Marine Specialties De-Oiling Ballast Water Preliminary Publication No. 1," Tretolite Treatment Program for Pollution Control and Hydrocarbon Recovery Method No. 2. Tretolite Division. Petrolite Corporation.
- 18. Anonymous. Danish Oil Destruction, Ltd. Norrel Lunchvij 12. Herlev. Brochure on "Absorption Media."
- 19. Ambrose, H. A. "Oil Pollution of Seas, Coasts, and Harbors," Petroleum Products Department Report No. 700R7001, Gulf Research and Development Company. September 1967.
- 20. Beynon, L. R. The TORREY CANYON Incident A Review of Events,"
 The British Petroleum Company Limited. September 1967.
- 21. Caldwell, J. M. "Oil Pollution of the Shore Face Caused by the TORREY CANYON Disaster," Coastal Engineering Research Center, Department of the Army. August 29, 1967.
- 22. Gall, D., T. A. Dorling, and J. W. Smith. "Improvements in or Relating to the Treatment of Mobile Substances Floating on Liquids," British Patent 979, 978. January 6, 1965.
- 23. Glude, J. B. and J. A. Peters. "Observation on the Effect of Oil from the Tanker TORREY CANYON and Oil-control Measures on Marine Resources of Cornwall, England and Brittany, France," submitted to Director, Bureau of Commercial Fisheries, June 1967, (unpublished).
- 24. Glude, J. B. and J. A. Peters. "Recommendations for Handling Oil Spills Similar to that from the Tanker TORREY CANYON," submitted to Director, Bureau of Commercial Fisheries, June 1967, (unpublished).
- 25. Henderson, J. B. Port Manager, Fort Everglades, Florida, Personal Communication.
- 26. Kondo, G., M. Hayoshi and Y. Murekami. "Studies on the Method of Collecting Oil From the Surface of Water," Osaka Industrial and Technological Laboratory, Quarterly, vol. 18, no. 1, pp. 35-39. May 1967. (In Japanese)
- 27. Lowell, F. B. Naval Ship Engineering Center Washington, D. C. 20360, Personal Communication, October 2, 1967.
- 28. Pleuss-Stauffer (North American), Technical Note TR-13-15.
- 29. Smith, J. W. "The TORREY CANYON Disaster," British Association for the Advancement of Science, Annual Meeting, Leeds, England, September 1967.

Addenda

30. Herbinger, P. J. "Composition for the Elimination of Hydrocarbons Floating on Water," French Patent 1,391,144. March 5, 1965.

- 31. Sturz, O. and K. Klein. "Testing of Building Media for the Removal of Oily Impurities in Surface Waters," <u>Deutsche Gewasserkund-liche Mitteilungen</u>, 8(6), pp. 127-138. December 1964.
- 32. Pilpel, N. "Oil Pollution of the Sea," Research, vol. 7, p. 301. 1954.
- 33. "Practices for Handling Major Oil Spillage," Standard Oil of California Letter from E. S. Warner. October 6, 1967.
- 34. Monsanto Chemical Co. and Dynasurf Chemical Corp., 'Development of Treated Sand Materials," The Baltimore Sun. March 31, 1967.

Patents on Absorbent Materials

- 35. Oil or Oily Residues Floating on the Surface of Water are Removed, F. G. Grunwalt & E. Arnt Neth. Appl. 222, 827 (4/16/63); f. Ger (11/28/56); Brit. 954, 797, f. 8/11/60
 Liquids or solids heavier than water.
- An Absorbent for Removing Oil Slicks from Water, O. Kappel Neth. Appl. 222, 426 open 7/16/62
 Solid particles coated with a carbonaceous material.
- 37. (In) Removing Hydrocarbons from the Surface of a Body of Water, E. Miquelis
 French 1, 315, 980 open 1/25/63
 1st Add. 81, 814 open 11/15/63
 2nd Add. 82, 383 open 1/31/64
 Powder plus wetting agents; Silica. etc.
- 38. Oil Floating on the Surface of Water is Removed, L. N. Goldsbrough & R. Graham
 Brit, 919,790 publ. 2/27/63
 Solid (fly-ash), free carbon-containing adsorbent.
- 39. Hydrocarbons Are Removed from Aqueous Surfaces, C. Ritter French 1,253,062 open 2/3/61
 Powdered Carbelim, mixture of carbon and two carbonates.
- Oil Floating on the Surface of Water is Removed, L. N. Goldsbrough & R. Graham
 Brit. 919,780 publ. 2/27/63
 Coal dust, spent catalyst or fly-ash and surface active agent.
- 41. Hydrocarbons Are Removed from Aqueous Surfaces, C. Ritter French Add. 79,169 open 11/2/62 to French 1,253,062 Mixture of calcium carbonate and an adsorbent clay.

Ţ

- Activated Carbon Used In the Deciling of Water Is Generated in Situ. E. Fisher Ger. Ser. 1,128,411 open 4/26/62 Add. to Ger. 975,244
- 43. Hydrocarbons Are Separated From An Aqueous Mixture, A. N. Oemeler U. S. 3,147,216 i, 9/1/64
 Poly-1-olefin fluff
- A Material Floating on the Surface of A Liquid Is Treated,
 D. Gall, T. A. Dorling & J. W. Smith
 Brit. 979, 978 publ. 1/6/65
- 45. A Pulverulent Material for Removing Hydrocarbons Floating on the Surface of Water, P. J. Herbinger French 1, 391, 144 f. 1/23/64
 Milled mixture of a dense mineral and naturally occuring rock, for example barytes and bauxite
- 48. Surface Oil Is Collected from Water, K. I. Wyllie & E. W. Duck U. S. 3,265,616 i. 8/9/66
 Brit. 992,524, publ. 5/19/65
 Application of latex, followed by coagulation with salt or acid.
- 47. Oil Is Removed from the Surface of Water, H. C. Anderson French 1, 400, 102 f. 7/1/64
 Neth. Appl. 64, 07689 open 1/10/66
 Tale mixed with chalk.
- 48. Oil Wastes Are Made Nontroublesome, H. H. W. E. Braun-Mutillet French 1, 388, 841 open 2/12/65

 Powdered water glass and an alkali metal chloride on a finely divided support; may also contain a polyglycol ether and an alkali metal carbonate or bicarbonate.
- 49. Absorbing Oil Floating On Water With Silicone Treated Expanded Perlite
 Deutsche Perlite, G. m. b. h.
 Ger. Ser. 1,195,220 open 6/16/65
 Neth. Appl. 65,04512 open 5/16/66
 French 1,425,641 f. 2/4/65
- 50. Mineral Oils, Fuels, and Other Organic Liquids Are Removed From Water, Grunzweig & Hartmann A. G. French 1,440,470 f. 7/16/65 Ger. f. 7/17/64 Oil absorbed by a plastic foam.
- An Absorbent for Removing Oil Floating on the Surface of Water, Neste OY
 Neth. Appl. 66, 13071 open 3/17/87
 Finland F. 9/16/65

 Clearing Water Surfaces of Oil W. A. Zisman and L. Pickett U. S. Patent No. 2, 447, 551 6/22/43

- 53. Yosemite Chemical Co., (E. R. Delew) U. S. Patent 3, 198, 731 8/3/65
- 54. Yosemite Chemical Co., (E. R. Delew and A. Lazar) U.S. Patent 3, 272, 758 9/13/66
- 55. Open Bottom Barge Oil Spill CollectorE. J. LaneU. S. Patent

4.3 CHEMICAL TREATMENT--DISPERSION

Following the TORREY CANYON disaster, the British made extensive use of detergents to emulsify oil floating on the open sea as well as oil deposited on beaches. Certain key references are directly quoted below, because they have had limited distribution but offer the benefit of direct field observation and careful assessment of control measure results.

Glude (16) reported that:

"Oil control activities of the French varied considerably from those of the British. After a brief trial the French Government established a policy of avoiding the application of detergents because of the adverse effect on marine resources and because of the difficulty of cleaning contaminated beaches. It was stated by the French authorities that the mixture of oil and detergent included up to 80% water thereby greatly increasing its volume and making it impossible to dispose of it by burning. Furthermore, the mixture tended to cover a beach on one tide and then on succeeding high tides to be carried to other locations so that eventually the entire intertidal zone of an area would be coated. In contrast, crude oil by itself is more likely to adhere high in the intertidal zone and to remain in that location.

"French authorities condemned the British for applying great quantities of detergent at sea, maintaining that this greatly increased the severity of the problem when the floating mixture reached the French coast. For these reasons, the French decided to use physical methods whenever possible for control of oil."

Glude and Peters (17) reported as follows:

"Immediately following the grounding of the TORREY CANYON detergents or solvent-emulsifiers were sprayed on the patches of oil from surface vessels or from the air in an attempt to disperse and emulsify the oil. It is estimated by the British that one half million gallons of detergent of many different formulations but 85% of which was BP-1002, was applied to the oil while it was floating at sea. The detergent changed the oil from a thick black mass to a chocolate brown mixture of oil, solvent-emulsifier and water. It is estimated by the French that 80% of this mixture was water. Although this application was partially effective in dispersing the oil, the French authorities maintain that the problem of disposal on shore

was aggravated because the mixture was much greater in volume than the original 118,000 tons of oil. The maximum volume of the mixture, including the oil, approximately 2,000 tons of detergent and water may have approximated 600,000 tons. The French stated further that the mixture was moved more rapidly by wind and wave action than oil alone and, therefore, was more apt to be carried great distances.

"It was also found by both the French and the British that the mixture was more difficult to remove once it had reached shore than crude oil by itself. Crude oil tends to stay on the surface of sandy beaches and forms balls which solidify into masses that can be removed mechanically. The mixture, however, coats the surface of the sand and then mixes with the sand particles to a depth of 12 in.

"Crude oil by itself is carried high on the beach by wave action and if deposited on rocks tends to remain there. The mixture, however, may be removed by the following high tide and carried to another location. This was especially evident along the North-West coast of Brittany where a heavy concentration of emulsion was deposited on relatively inaccessible offshore islands but later was carried to the mainland where it re-contaminated previously cleaned beaches.

"Although the ignition point of crude oil is rather high, it can be burned whereas the mixture containing an estimated 80% of water is not combustible. Crude oil is reportedly destroyed gradually at sea by bacterial action but it is unlikely that this would occur with the mixture since the solvent emulsifier inhibits bacterial action.

"Under certain circumstances, such as when limited amounts of oil are spilled within protected bays or harbours, it may be appropriate to use detergents along with other control measures, such as encircling the oil with booms. In Milford Haven, England, where there are frequent oil spills from the three large oil company operations there, a regular plan has been established for oil centrol. This consists of prompt installation of booms to prevent spread of the oil, pumping to remove as much as possible and the judicious application of limited amounts of detergent. These control methods are reported to be quite successful but can only be applied in protected waters and where control facilities are readily available. It is much more likely that disastrous oil spills of the

magnitude of that from the TORREY CANYON will occur on rocky headlands or exposed beaches where wave action in usually great and more probably during periods of adverse weather costic s."

Concerning sandy beaches, G. and Peters further reported:

"The high waves prevalent on exposed sandy beaches make it difficult to carry out physical methods of controlling or containing oil spills so it is better to let the oil come ashore where it can later be removed preferably by physical means. Untreated crude oil tends to form balls when it is mixed with sand by wave action. These balls of oil and sand harden and can later be removed physically. In contrast, oil mixed with detergent tends to penetrate the top 10 to 12 in. of sand and becomes rather evenly distributed or present in thin layers which makes physical removal difficult."

Beynon⁽¹²⁾ reported findings similar to Glude's:

"In principle it is better to remove oil from a beach rather than to emulsify and disperse it into the sea using detergent and water, and only where physical removal is not practicable should detergent be used.

Because the nature of both pollution and beaches varies greatly from one place to another, it is not possible to recommend any methods which would by universally applicable. The best way to deal with oil pollution in any particular place must be decided on the spot, and the decision is also influenced by what mechanical equipment is available.

"In some instances it is possible to use a bulldozer to skim off a surface layer of sand and oil. This should then be removed from the beach and disposed of, or at least moved above high tide mark for subsequent disposal or incineration. Where oil spots or balls of oil and sand are widely dispersed, the surface sand may be pushed into windrows using wooden squeegees and the windrows bulldozed up and removed. Where such oil spots and balls of oil and sand are left at a tide mark it is often possible, as an alternative, to remove them with shovels or by hand. These methods of physical removal of the oil are usually limited to instances where the oil is on or near to the beach surface. Where an oil/sand mixture is deep, the amount of sand which has to be removed with the oil magnifies the task of physical removal and disposal to impracticable proportions, especially

as many beaches need to retain all their available sand. Where an oil layer has not mixed with sand but has become buried under a deep layer of clean sand, it is possible to bulldoze the clean sand away thus exposing the oil and allowing it to be removed as for surface oil; the clean sand may then be bulldozed back into position.

"Even if it is only feasible to remove a portion of the offending oil from a beach by physical means, this should be undertaken to lessen the subsequent task of emulsifying and dispersing it in the sea.

"By far the quickest and most successful means of using detergent to clean a sandy beach which has r. layer of oil contamination at or near the surface, involves the use of an agricultural rotary cultivator. The cultivator is towed behind a tractor and set to rotavate the top six inches of oil and sand, thus breaking-up the oil and mixing it with clean sand. Detergent is sprayed from the tractor on to the oil and sand during rotavation. Where a beach is 'wet' and the applied detergent remains mixed with standing water near the sand surface, further spraying is usually unnecessary. On normally 'dry' beaches, the beach should be re-sprayed with detergent from a tractor across the advancing tide. This method has been successful in virtually cleaning beaches completely in a single application. The only pollution that is normally left consists of walnutsized balls of oil deposited on the high tide mark. These should preferably be physically removed but, alternatively, rotavating/deterging of a narrow strip along the tide mark prior to the next high tide is usually sufficient to disperse the last traces of oil.

"On a beach where the oil has sunk into the sand, it is also possible to greatly reduce the amount of oil present by deterging the sand and bulldozing the layer of oily sand into the sea at low water. The cleansing action of the sea disperses the oil leaving a comparatively clean beach, although the procedure may have to be repeated several times to achieve complete success.

"The chief trouble with cleansing r beach to any depth using detergent and mechanical equipment is that it leaves the beach soft and soggy and extremely difficult to work on in the event of subsequent pollution. A beach which has been soaked with detergent also feels and smells

objectionable, and most complaints of the stench of oil on beaches in Cornwall stemmed from the presence of detergent rather than that of the polluting oil.

"Detergent must never be applied to sand without turning over the oil/sand mixture and following with a water wash within one hour. The result of spraying oily sand with detergent in the absence of water is usually to cause the oil to penetrate deeper into the sand thus greatly increasing the problems of clearance.

"Oily shingle beaches offer a somewhat different problem to that presented by contaminated sandy beaches. Rotary cultivators cannot be used on coarse shingle (pebbles). The quickest methods of clearing a shingle beach are to spray with detergent immediately ahead of the advancing tide or to spray and immediately bulldoze the contaminated shingle into the sea. Again it is essential that a deterged shingle beach should be washed by the sea within an hour of deterging, otherwise the oil may penetrate very deeply into the shingle.

"Whether on sandy beaches or on shingle, the method of detergent application is most important. Detergent must be sprayed onto the polluted area and not just pumped or poured on. Ideally, for speed of application, the detergent should be sprayed from, say, a 6 ft long pipe fitted with spray nozzles and fed from a 40 gal. drum via a high pressure pump and a light hose. The spraying equipment should be mounted on a tractor or trailer. In an emergency, however, a great deal may be achieved using available equipment and a little ingenuity. For example, one enterprising local authority engineer used a 1/2 horse power pump to feed detergent to a 100 ft length of garden hose perforated with 1/16 in. diameter holes at 6 in. intervals. Towing this hose behind a tractor across the advancing tide he successfully cleared a small shingle beach of pollution in under half-an-hour."

Smith (23) reported:

"A good deal of work on the choice of the emulsifying agent was carried out at Warren Spring Laboratory, and the Admiralty Oil Laboratory also carried out similar work. In general a nonionic emulsifier, particularly a nony phenol ethylene oxide condensate, appears

to be the best type and the diluents or solvents which gave the best results were those containing a high proportion of aromatic hydrocarbons such as the aromatic solvents with a boiling range between 170 to 220 °C.

"It was found that between 10 and 20% of the emulsifier was required in the hydrocarbon solvent. In the ideal case the choice of the emulsifier will depend upon the oil to be emulsified. Some of the commercial mixtures which are available use a single emulsifier, others use two or even three. To make a satisfactory emulsion of floating oil under carefully controlled conditions, it takes something like 10 to 20% of the solvent emulsifier mixture. (In a beaker with efficient agitation much less is wanted). Under conditions at sea this can run up to 100% or even more. The problem, of course, is to get the right amount of the solvent emulsifier to each small area of the oil. The thickness of the oil layer can vary considerably over short distances so it is impossible to apply just the right amount. Also after allowing sufficient time for the solvent to carry the emulsifier into the oil, sufficient agitation must be given to form the emulsion. All of this is, under open sea conditions, a hit and miss affair. Nevertheless when conditions are satisfactory this is a most effective way of dealing with oil spills and it has been used for the past few years in the major oil terminals of the British Isles."

In further discussion of oil dispersion, Smith stated:

"This has been shown, for very much smaller amounts of oil, to be an entirely successful method when properly carried out. Now in retrospect it might well have been better to have attempted to collect the liquid oil on the beaches by mechanical means, or even by hand as there was plenty of service labour available, before carrying out the solvent emulsifier treatment. The result might well have been obtained more quickly and the damage, or potential damage, to the flora and fauna on the inter-tidal zone would undoubtedly have been reduced. The treatment of the water in oil emulsion, the 'chocolate mousse', was very much more difficult. Fortunately a great deal of this did not appear on the British coast, the coasts of Brittany and Guernsey having the major proportion."

Caldwell, (13) in reporting on observations in Britain and France, suggested that the amount of oil actually removed by detergent is problematical. He further indicated that on the order of 15 to 20 gal. of detergent were used per front-foot of beach in one instance at Porthmere.

Smith (23) pointed out:

"There is one feature of the TORREY CANYON incident which differed very considerably from the majority of other oil spills. This was the appearance of large quantities of emulsified oil, not the desirable oil-in-water emulsion but a thick, water-in-oil emulsion. This material, which contained up to 70% of water, had a specific gravity very close to that of water so that in fact it tended to float just below rather than on the surface. This came ashore in large quantities and was commonly referred to as 'chocolate mousse', which it closely resembled in appearance. The particular properties of the crude oil, which came from the TORREY CANYON, containing as it did asphaltic and resinous particles, favoured the formation of a water-in-oil emulsion. This was probably stabilized by external agents such as bacterial slime, plankton and organic debris. This material was almost impossible to deal with on the sea and was very much more difficult to deal with when it landed on the beach."

The "chocolate mousse" was allowed to come ashore on the Brittany coast where it was collected by hand labor rather than treated with detergents. The extent to which the "mousse" formed naturally from the crude is not clear. The French attributed its formation to the detergents employed by the British, although Beynon (12) reported that Kuwait crude oil and natural seawater can form this without detergent present.

The British used several detergents, but the product used most often was "BP1002", a British Petroleum Ltd. product (sulfonated dodecyl benzene in kerosene). Dudley (14) reported that detergent in the amount of at least 50% of the oil volume was required to remove the oil and that of all methods used to clean beaches, the successful treatment always involved the use of detergents. This opinion is in contrast to those previously noted from Glude, Beynon, and Smith. Applications of detergent was followed by agitation with sea water jets.

Dudley further reported effective treatments as follows:

On Sandy Beaches. The beach should be ploughed or buildozed into furrows on the ebbing tide and detergents sprayed onto the disturbed sand in front of the incoming tide. Another method is to treat the sand with dispersant and then buildoze approximately the top 3 ft into the sea.

On Shingle Beaches. The beach should be sprayed with dispersant and hosed vigorously towards the sea, or sprayed with dispersant and allow the incoming sea to provide the vigorous mixing. Bulldozing the top layer into the sea was also tried with shingle beaches.

On the Rocks. Rocks should be sprayed with dispersant in front of the incoming sea. Unfortunately, this is usually difficult on rocky coasts, because rocks are not easily accessible; therefore, this desirable method can seldom be adopted in practice. Helicopters dropped 45-gal. drums from a height of 200 ft onto the rocks in inaccessible positions so that they burst on impact. This is obviously a very expensive and wasteful method, but is sometimes the only one available. Some success was realized by cleaning rocks with steam.

Dudley suggested that it may have been a cheaper treatment to remove the top 2 or 3 ft of beach sand before the oil arrived, then use this sand to cover the deposited oil. This is of doubtful value because later wave action will resurface the oil and biodegradation and natural weathering is hindered when the oil is buried. Taylor (24) reported that large quantities of solvent carriers (frequently an aromatic solvent) are required in order to distribute the surface-active emulsifying agent throughout the oil, and that quite inadequate mixing is achieved by using water jets or propellers. Taylor also provides an outline of standard tests employed by Esso Petroleum Co. Ltd. for solvent-emulsifiers. These tests include a beach cleaning efficiency test and an emulsion stability test and are apparently similar to those employed by the Warren Spring Laboratory. (1)

Hellman^(18, 19) has carried out tests on emulsifiers. Thirteen proprietary materials of German manufacture were tested for effectiveness, for degradation behavior, and for biological effects. A lubricating oil and a fuel oil were used in separate tests with sea, tap, and distilled water. Initial and 14-day emulsion stabilities were observed and compared.

Emulsifying capacity was determined, and emulsion stability was noted as a function of time and emulsifier concentration. The effects of temperature and pH were determined. Biochemical oxygen demand was determined over a 30 day period and rates of biochemical assimilation of oil was observed.

Hellman points out that excess emulsifier always enhances its performance but also increases its toxicity. All emulsifiers investigated were "nontoxic" at concentrations of 5 to 10 mg/liter.

The U.S. Navy has established a specification (MIL-S-22864, SHIPS, March 28, 1961) covering an oil-slick solvent emulsifier. This specification (amended April 11, 1966) includes a standard test and evaluation procedure.

Table 4.3-1 presents a representative list of emulsifiers for dispersion of oil. Indicated also are the present sources of supply along with pertinent remarks. The majority of these products are the result of proprietary development by the manufacturer involved and the chemical composition cannot be obtained without careful chemical analysis. In any event, it is expected that the majority are closely or generally related and can be expected to show similar properties. No definitive or quantitative data or scientific evidence relating to their relative performance or toxicity was identified in the course of this study. A supplementary bibliography is attached giving reference to largely nontechnical discussion.

In summary, although some disagreement exists, there is substantial evidence which supports the view that emulsifying detergents can cause problems both practically and ecologically in excess of those created by deposition of the oil alone. For example, no quantitative evidence was uncovered to indicate that any detergent had zero or even a low order of toxicity. Based on this and the evidence gained through abundant field observations, it is concluded that collection techniques are by far the most acceptable methods for controlling major oil spills.

Detergent materials may have use in controlling small oil spills under carefully controlled conditions with advance knowledge of effects. The observations made on the Coast of Cornwall, where excessive use of detergents was made, suggest that at best detergents are only partially effective despite heavy doses and at high cost.

	TABLE 4.5-1. Emulsifiers For Oil Dispersal	Dispersal
Product	Sources of Supply	Remarks
Actusol T-776	Dubois Chemical Company, Cincinnati	\$2.50/gal. satisfactory performance (Shell, Reference 9)
BP-1002	British Petroleum, Ltd.	Used in TORREY CANYON clean-up Sulfonated dodecyl benzene in kerosene Cost, \$1.20/gal. (Reference 11,13)
Dispersal Foilzoil Nighty Mate	Sea-Air Chemical Corp. 32-00 Borden Ave. Long Island City, New York 11101	
Essolvene	Esso Research and Engineering	(Reference 11)
Fina Unisol Fina Tar Solvent ES	Petrofina Great Britain U.K.	(Reference 4)
Gamlen-D Gamosol	Gamlen Chemical Co. 321 Victory Ave. San Francisco, Calif.	(Reference 11)
Gulfsil de-greaser	Gulf Oil (Great Britain) Ltd. 6 Grosvener Place London, S.W.1	(Reference 24)
Groeskilla 3	Atlas Preservative Co. Erith, Kent, England	(Reference 24)
Houghtosolv	Edgar Vaughan and Co. Ltd. Leggo Street Birmingham 4, England	(Reference 24)

BATTELLE NORTHWEST

Tokyo, Japan

4-38

TTELLE NORTHWEST

TABLE 4.3-1. (Contd)

BATTELLE - NORTHWEST

į

(Contd)	
TABLE 4.3-1.	Comments of Comments

Remarks	\$3.25/gal., good performance and stability (Shell Reference 9)	Approximately \$2 to \$3.00/gal. (Reference 6)
Sources of Supply	National Research and Chemical Co. Hawthorne, California	Petreco Corporation Tretolite Div. 369 Marshall Ave. St. Louis, Missouri 63119
Product	TYFO-80	Various Proprietary

DuBois Chemical Co. Cincinnati, Ohio

Aquanix, F.O. 300, Mabec, P.P. 5 and XZIT

No Name Given

Literature Cited Concerning Chemical Treatment--Dispersion

- 1. Anonymous. The Treatment and Disposal of Floating Oil, Warren Spring Laboratory, Ministry of Technology, United Kingdom, Report No. RR/ES/40. April 1963.
- 2. Anonymous. "A New Organic Complexing Agent from Guardian Chemical Disperses Oil Droplets," Chemical & Engineering News, p. 49. July 10, 1967.
- 3. Anonymous. "The Wreck of the TORREY CANYON," Chemical Week, p. 59. April 8, 1967.
- 4. Anonymous. "Combatting Oil Pollution," Petrol. Times, vol. 71, pp. 627-628. April 28, 1967.
- 5. Anonymous. "Mopping up Oily Oceans," Time, p. 68. July 28, 1967.
- 6. Anonymous. "Marine Specialties De-Oiling Ballast Water Preliminary Publication No. 1," Tretolite Treatment Program for Pollution Control and Hydrocarbon Recovery-Method, No. 2, Tretolite Division, Petrolite Corporation.
- 7. Anonymous. "Clearing Gross Oil Pollution," The Marine Engineer and Naval Architect, p. 474. April 1961.
- 8. Anonymous. "Oil Pollution Killed in Open Water," Brit. Chem. Eng., vol. 6, p. 244. April 1961.
- 9. Anonymous. Informal Shell Oil Co. summary sheet.

'a e,

- 10. Anonymous. Correspondence and Brochures on Polycomplex A, Guardian Chemical Co.
- 11. Ambrose, H. A. Oil Pollution of Seas, Coasts, and Harbors, Petroleum Products Department Report No. 700R7001, Gulf Research and Development Company. September 1967. (Extensive bibliography)
- 12. Beynon, D. R. The TORREY CANYON Incident A Review of Events, The British Petroleum Company Limited. September 1967.
- 13. Caldwell, J. M. Oil Pollution of the Shore Face Caused by the TORREY CANYON Disaster, Coastal Engineering Research Center, Department of the Army. August 29, 1967.
- 14. Dudley, B. L. Report on Harbor Master's Visit to Cornwall to Study Anti-Pollution Measures. April 25, 1967.
- Globus, W. P. Director of Research, Guardian Chemical Co., Letter to Natural Wildlife Federation.

- 16. Glude, J. B. and J. A. Peters. Observation on the Effect of Oil from the Tanker TORREY CANYON and Oil-Control Measures on Marine Resources of Cornwall, England and Brittany, France, Submitted to Director, Bureau of Commercial Fisheries.

 June 1967 (unpublished).
- 17. Glude, J. B. and J. A. Peters. Recommendations for Handling Oil Spills Similar to that from the Tanker TORREY CANYON, Submitted to Director, Bureau of Commercial Fisheries.

 June 1967 (unpublished).
- 18. Hellmann, H., et al. "Investigations into the Suitability of Emulsifying Agents for the Elimination of Oil on Water Surfaces," Sonderdruck Auf Deutsche Gewässerkundliche Mitteilungen, 10(2, 3), pp. 29-35, 60, 70. April & June 1966.
- 19. Hellmann, H., et al. "Further Investigations into the Suitability of Emulsifiers for Elimination of Oi? from Surface Waters,"

 Deutsche Gewässerkundliche Mitteilungen, 11(4), pp. 91-95.

 July 1967.
- 20. Krugel, R. A. "Oil Slicks Treated with Emulsifying Chemicals," World Ports and Marine News. January 1966.
- 21. Lowell, F. B. Personnel Communication. Naval Ship Engineering Center, Washington, D.C. October 20, 1967.
- 22. Robinson, K. Demonstration of Polycomplex A, Bureau of Commercial Fisheries. July 6, 1967.
- 23. Smith. J. W. "The TORREY CANYON Disaster," British
 Association for the Advancement of Science Annual Meeting,
 Leeds, England. September 6, 1967.
- 24. Taylor, J. C. J. Inst. Petroleum, vol. 48, p. 355. November 1962.

Supplemental Bibliography

- 1. Business Week, p. 184. April 22, 1967.
- "Deleterious Effects of Emulsifiers," Chemistry, vol. 40, p. 8. October 1967.
- 3. Chem. Brit., vol. 1, p. 240. June 1965.
- 4. "New Dispersant Controls Oil Pollution," Chemical Engineering, p. 112. May 22, 1967.
- 5. Chemical Week, p. 49. May 20, 1967.
- 6. "The Wrec' of the TORREY CANYON," Chemical Week, p. 59. April 8, 1:

- 7. "How to clean an Oily Beach," Chemmunique, 14(1), pp. 5-6. Februar 1965.
- 8. "Chemic s vs. Crude Oil," Chemical Week. May 20, 1967.
- 9. "Confine nent and Removal of Oil," IMCO (Intergovernmental Maritime Consultive Organization). October 16, 1967.
- 10. "Test of Straw as an Absorbent," International Oceanographic Foundation, p. 5. September 1967.
- 11. "Pollution by Oil . . .," Marine Engineering/Log, pp. 42 and 87. June 1967.
- 12. "Clearance of Oil Pollution," Petrol. Times, vol. 65, p. 508. August 25, 1961.
- 13. Petrol. Times, vol. 71, p. 627. April 28, 1967.

第五番を持ち込むまででいるます。 かんてきないながら、まちゃっきのとうことをものいないます。 あらずる

- 14. "Three Methods of Combatting Oil Pollution," Petrol. Times, vol. 66, p. 293. May 4, 1962.
- 15. "Cleaning Up Oil Pollution at Sea," Science News, p. 429. May 6, 1967.
- 16. Grunwalt, G. and E. Arnt. "Removal of Oil and Oil Residues from Water Surfaces by Treatment with One or More Soluable Groups III, VII or VIII Metal Salts and a Wetting Agent," German Patent, No. 1,113,187. August 24, 1964.
- 17. Hoffman, R. E. Public Works, N.Y., vol. 80, p. 26, 1949.
- 18. Pilpel, N. "Oil Pollution of the Sea," Research, vol. 7, p. 301, 1954.
- 19. Sigwalt, R. "The Forces Causing Spreading of Petroleum Products on Water and Their Neutralization by Fatty Oils," Compte. Rend., vol. 259, p. 561. July 20, 1964.
- 20. Warner, E. S. "Practices for Handling Major Oil Spillage," Standard Oil of California, Letter of October 6, 1967.
- 21. Valentin, F. H., et al. "Coagulants & Demulsifiers," Chem. Ind. (London) no. 51, p. 1976. December 21, 1963.
- 22. Zisman, W. A. and L. Pickett. Wetting and Spreading Agents for Clearing Water Surfaces of Oil Films, NRL Report No. P-1930. September 9, 1942. Also U. S. Patent 2,447,551.

4.4 BIOLOGICAL DEGRADATION OF CRUDE OIL AND OIL FRACTIONS IN THE OCEAN

A significant question posed as the result of the TORREY CANYON incident is the following: If no measures were taken to remove oil spilled on the surface of the ocean, how long would oil persist? In particular, could the interobiological life in the sea metabolize oil, and if so, at what rate? ZoBell⁽⁵⁾ has spoken to these points at great length. His paper represents what must be regarded as the most complete compilation of information on this subject.

ZoBell concludes that, "Virtually all kinds of oil are susceptible to microbial oxidation. The rate of such oxidation is influenced by the kinds and abundance of microorganisms present, the availability of oxygen, temperature, and the dispersion of the oil in water. Microbial oxidation is most rapid when the hydrocarbon molecule is in intimate contact with water and at temperatures ranging from 15 to 35 °C; some oxidation occurs at temperatures as low as 0 °C. An average of one-third of the hydrocarbon may be converted into bacterial cells, which provide food for many animals. The remaining two-thirds of the hydrocarbon is oxidized largely to CO_2 and H_2O . In the marine environment, oil persists only when protected from bacterial action.

"Based upon rates at which marine bacteria have been observed to oxidize various kinds of mineral oils under controlled laboratory conditions and upon information on the abundance of bacteria in the sea, it is estimated that oil might be oxidized in the sea at rates as high as 100 to 960 mg/m 3 day or 36 to 350 g/m 3 year."

Smith (4) has taken issue with the rates of oxidation of oil estimated by ZoBell. Smith claimed that laboratory experiments showed that the rates may be a high estimate. Nevertheless, it is widely recognized that oil can be metabolized in the ocean. Even if ZoBell's estimates are accurate, it is evident that oxidation rates are slow. Prokop (3) has conducted experiments which graphically demonstrate that even when acclimated cultures of microorganisms are used in decomposition studies, extended periods of time are required for complete degradation. Prokop believes the presence of acclimated cultures are critical to the degradation of crude oil.

On the other hand, Ludzack⁽¹⁾ has concluded that common microorganisms found in surface water are capable of biologically oxidizing motor oil. Seed from several petroleum-polluted sources was used, but sewage was more effective than any other inocula. With 10 percent sewage in an oil emulsion, CO₂ production increased for about 10 days, then decreased to almost zero at 28 days. Reseeding with sewage restored oxidation to maintain a rate of hydrocarbon decrease of 50% per week. It was necessary to add 1 percent of sewage per day. There was a marked difference in the types of biological organisms depending on the frequency of seeding. The principal end product of oil oxidization is carbon dioxide. The most prominent intermediate compounds are organic acids and esters. A related conclusion of another study is as follows: "Hydrocarbons can be decomposed by biological action in the presence of suitable seeding material and with adequate nutrient supplementation by nitrogen, potassium, and phosphorus. Oxygenated derivatives decompose readily." (2)

In summary, if environmental conditions, (nutrients, temperature, oxygen availability) are satisfactory, and if suitable microbial populations are present, oil will be degraded in the ocean. However, the rates of hydrocarbon degradation are slow when compared with those of the oxygenated derivatives. There has been much speculation recently about the ability of highly specific cultures to rapidly degrade oil spills, yet a dearth of specific information is evident.

Literature Cited Concerning Biological Degradation of Crude Oil

- 1. Ludzack, F. J. and D. Kinkead. "The Persistence of the Motor Oil Class of Hydrocarbons in Polluted Water Under Aerobic Conditions," Presented before the 127th National ACS Meeting, Cincinnati, Ohio. April 4, 1955.
- 2. McKee, J. E. Report on Oily Substances and Their Effects on the Beneficial Uses of Water, Publication No. 16, State Water Pollution Control Board, Sacramento, California. 1956.
- 3. Prokop, J. F. Report on a Study of the Microbial Decomposition of Crude Oil, Texas A&M Research Foundation, Project 9, (mimeo).

 1950.
- 4. Smith, J. W. "The TORREY CANYON Disaster," Annual Meeting, 1967, British Association for the Advancement of Science. September 6, 1967.
- 5. ZoBell, C. E. "The Occurrence, Effects and Fate of Oil Polluting the Sea," Int. J. Air Wat. Poll., vol. 7, pp. 173-198. 1963.

4.5 BOOMING

There are three general classes of barriers that can be used to prevent the spread of oil on the surface of the water. These include floating booms, underwater bubble barriers, and chemical booms. In their present state of development, all types will at best retain or stop the spread of oil only in relatively calm waters with little current.

4.5.1 Mechanical Booms

Floating booms are presently in common use for the control of oil spillage in many harbors where transfer operations take place. There are several commercial designs available as well as makeshift methods such as inflated fire hoses. In general, all mechanical booms have a floating section consisting of either an inflatable bladder or a buoyant filler material such as foamed plastic. Below the floating section is some form of skirt to which ballast or anchors are attached. The floating booms are used for such operations as confining oil within an area, preventing the spread or passage of oil, sweeping oil from a particular area, or condensing a slick into a smaller area.

Oil slicks on the water have a mean surface elevation that is higher than the elevation of the water surface outside of the slick. A floating slick will have a difference in elevation, or freeboard, with respect to the surrounding water surface according to the equation:

$$FBD = \left(1 - \frac{\epsilon_0}{w}\right) T$$

where,

FBD = difference in elevation, freeboard

fw = density of water

vo ≈ density of oil

T = thickness of oil slick.

Similarly, the oil-water interface will be depressed below the surrounding surface to a draft equivalent of:

$$D = r_0/r_w T$$

For the case of a typical United States crude oil floating in sea-water

$$\rho_{\rm W} = 1.035 \, {\rm gm/cm}^3, \ \rho_{\rm O} = 0.855 \, {\rm gm/cm}^3$$

Therefore.

FBD =
$$\left(1 - \frac{0.855}{1.035}\right)$$
 T,

and the draft of the slick,

$$D = 0.83 T$$

This means that the boom will require a minimum freeboard of approximately 1/5 and a minimum draft of about 4/5 of the thickness of the slick to contain the oil in calm conditions. It can easily be seen why so many makeshift booms without skirts fail by passing the oil underneath.

Following the TORREY CANYON stranding, several desperate efforts were made to construct booms of any material immediately available to keep the oil from reaching beaches and estuaries. Dudley⁽⁵⁾ reported that the following make-shift booms were tried:

- (1) "Antisubmarine-net equipment, wrapped in Hessian, with buoys or oil drums inside the wire-to-provide flotation. These were used both as booms across estuaries and towed between two motor boats in the form of an oil sweep. Great difficulty was found in mooring these booms and they were proved to be exceedingly vulnerable to damage. It is doubtful if they were of any great use and all have now either been withdrawn or were destroyed."
- (2) "Timber barriers for closure of small harbours where the wave height did not exceed 2 ft. These booms were made up of lengths of 15 to 20 ft and were of timber of 10 to 14 in. square, the gaps between each baulk of timber being wrapped in canvas or Hessian. These booms were not found to be of any value as sweeps but were relatively successful in closing off small inlets."

- (3) "Oil drums wrapped in Hessian. These were used for closing small gaps but were found to be extremely difficult both to secure the drums one to the other and also to moor them, and they are not recommended."
- (4) "Lengths of 36 in. conveyor belting weighted on one side and supported by drums. This boom was developed by the English China Clay Company and was used in the Fowey River. It appears to be a relatively good type of temporary boom, but since the oil did not reach Fowey the boom has not been tested but this would appear to be a worthwhile system to be considered if booms were required hurriedly for temporary closing of off-shoots to the Haven."
- (5) "Holman Air Boom. This is a submarine line through which compressed air was passed which provided an air bubble barrier and was laid in the Helford River. No oil reached the Helford River and, therefore, the efficiency of this type of boom is not known. It is understood that a similar type of apparatus is being used at a BP installation in Libya and might be worth further investigation."
- (6) "Aeroprene Boom. This boom, which consisted of approximately 30 ft lengths of Aeroprene sponge and cost \$6 per ft, was found to be unsatisfactory for the following reasons:
 - · It gradually sank as the water impregnated the foam.
 - · It was virtually impossible to moor in its present form.
 - · It was difficult, if not impossible, to fit a skirt.
 - Having become heavily contaminated, it was extremely difficult to clean and, although expensive, might only be suitable for one operation.

The following custom-made booms were used:

(1) "Slick-Bar. This is a proprietary boom which has been used in this Haven and which was bought for St. Ives. It is extremely easy to handle and is very light, but it is extremely vulnerable and the joining of one unit to another is not satisfactory. It is therefore, not for use as a sweep and its uses are somewhat limited. Experience in Cornwall has shown that it can only be used in smooth water. I understand it was destroyed in a moderate gale the day after I left St. Ives."

(2) "Warne Boom. This is the type of boom which was used by Esso in Milford Haven originally and was inflatable. Improved types have now been developed which do not require inflation and which are not quite so prone to damage. The general impression in Cornwall is that this is the best boom but it is expensive (approximately \$8 per ft) and even it has not been found to be suitable if strung across a tide of more than 1-1/2 to 2 knots."

Dudley further summarized: "No booms tried in Cornwall were wholly satisfactory and all the home made types of booms were very vulnerable to damage and only lasted a few days in anything but very sheltered situations. The best type of boom was the 'Warne' boom which is expensive, but even it was only successful where the mooring arrangements were particularly good and where the tidal flow was small and the sea conditions were in its favour."

One boom developed as a result of the TORREY CANYON incident consumes oil while it acts as a floating barrier. (5) The floating portion is packed with fibrous polypropylene material which has a strong affinity for oil but does not absorb water. About 20 lb of fibrous material is contained per year and is capable of absorbing up to 6 times its own weight in oil. It is reported that a 75 yard long prototype has an oil capacity of about four tons.

Douma⁽⁶⁾ observes that the British originally planned to contain the oil in the vicinity of the TORREY CANYON with a boom made of expandable neoprene blocks similar to those that had been used successfully in the Arabian Gulf. Such a boom had never been tried on the high seas. Due to weather conditions, the decision was made not to use this boom and it was later placed in relatively calmer coastal waters where it proved unsatisfactory. ⁽⁸⁾

Douma further states:

"One of the major difficulties in dealing with floating oil is its great mobility due to the pronounced effect which wind, current, and waves have on its behavior. Relatively small quantities of oil, of the order of a few tons, can spread rapidly over a wide at of open water and become distributed as small individual oil patches which are n constant motion even in a moderately calm sea. Large quantities of oil may remain as a coherent patch or raft but

will still be in constant movement. The thickness of oil films can vary from a very thin monolayer-type film to one several millimeters thick, depending upon prevailing sea conditions and viscosity of the oil. An encircling boom would confine the oil in a relatively small area, thereby improving salvage or burning operations."

"In summary, neither the English nor French have developed a boom which will contain oil except in relatively quiet waters. Massive booms with great strength and heavy anchors are required to withstand normal waves and tidal currents which occur along most shores. Extensive research is required to develop booms or barriers which will effectively confine oil along shore and in the open sea under normal conditions of waves and tidal currents. One possibility is the development of a bubbler system type of barrier capable of controlling the movement of oil slicks."

The following general observations about booms were made by Dudley after an inspection tour.

- (1) "A successfully anchored floating boom floating at right angles to the wind or tide may delay the ingress of thin oil films, but it seems unlikely that it causes any appreciable delay in the passage of a substantial film (over 1/100th in.) because as the wind or tide brings the oil to the boom, the oil must either accumulate there or flow underneath. It accumulates and thickens up, and it has been found that it can reach a thickness of 5 in, in ten minutes and even this is based on its being spread over a 10 ft width. At this stage the oil will be dragged under the boom by the tide, considerable thicknesses are seldom trapped."
- (2) "Booms used as sweeps can be useful, but, here again, the quantities which they are capable of handling is relatively small and unless some suitable method can be found for removing the oil so collected, and this has not yet been done, the use of booms as a sweep have rather limited applications."
- (3) "Although anything that sits on the water surface is better than nothing, a circular cross-sectional boom is not as good as an angular one."

- (4) "In seas in excess of 2 to 3 ft even the best type of boom permits oil to slop over the top.
- (5) "If booms are being considered to protect beaches, the presence of an inshore wind inevitably means that the boom will do no more than delay the oil getting to the beach, but where the boom is placed across the mouth of an estuary where the current reverses every 6 hr and thereby takes the accumulative oil away, they have met with some success."
- (6) "In a 1-1/4 knot tide, booms with a nine inch emersion are relatively efficient, but if the tide exceeds 1-1/4 knots, some anchoring of the skirt is necessary to stop the boom from curling up. This greatly complicates the mooring arrangements."

Glude (9) reported that several booms were developed and tested at the Roscoff Marine Laboratory in France. The most satisfactory was a burlap tube filled with straw from 12 to 15 in. in diameter that was packed around polyurethane blocks about 6 in. square and 2 ft long. The sections were held together with a continuous synthetic fiber line of about 5/8 in. diameter.

Commercial and make-shift booms are now in usage at practically all marine terminals of the United States and Europe, particularly where oil transfer operations take place. They are either placed around ships during cargo-transfer-routinely-to prevent spread if a spill occurs or are quickly available in the event of an emergency.

The most satisfactory are those which can be stored compactly on the water and are self-buoyant.

4.5.2 Bubble Curtain Barriers

Compressed air distributed from a submerged pipe causes local upwelling with a resultant surface current flowing in both directions normal to the bubble curtain. As long as this net flow toward the oil is not exceeded by the free stream current or overcome by the wind force on the oil, the barrier will contain a spill.

Underwater bubble barriers are a relatively recent development and presently in use in the harbors of Hamburg, Germany and Tobruk, Libya (4) to help prevent the spread of oil from routine loading and unloading operations. Following the TORREY CANYON incident, a 1200 ft-long bubble barrier was placed across the mouth of the Helford River to try to prevent incoming oil. Performance is unknown as oil never reached this boom. (5) The present units use air up to 100 psi supplied by a compressor which makes the unit somewhat susceptible to mechanical failure. A rapidly deployable system could be developed employing a submerged, perforated, flexible base buoyed at the surface and supplied with air at a pressure sufficient to create critical flow through the perforations.

This type of barrier appears to have considerable merit for fixed installations in sheltered waters and has the advantage that entry and egress of ships is unimpaired.

A system based on the bubble curtain is being marketed in Sweden. $^{(10)}$

4, 5, 3 Chemical Booming

There has been relatively little study on the possibility of enhancing or preventing the spread of oil on the water surface by use of wetting or spreading agents. Ambrose (1) states, "Langmuir showed that hydrophobic (water-hating) hydrocarbons do not spread well on water, but that hydrophilic (water-loving) hydrocarbon derivatives spread well. This principle is used in putting cetyl alcohol on reservoir water to retard evaporation. The cetyl alcohol is hydrophilic and forms a continuous, thin, nonvolatile film on the surface of quiet water. Wind and wave action may disrupt the film and push it down wind however.

"Addition of relatively small proportions of a hydrophilic compound (stearic acid, or oleic acid or other hydrophilic compound) to oil may cause the oil spill to spread over a vast area. Oxidation and bacteria action will' be enhanced by such dispersal.

"On the other hand, if fatty acid is spread at the periphery of an oil spill the spreading force of the fatty material will repel the nonpolar petroleum oil and push it into a smaller area. This latter means of containing an oil spill is discussed by Sigwalt. (2)...

Some experimental work by the Naval Research Laboratory was reported by Zisman and Pickett⁽³⁾ on tests made on wetting agents as well as spreading agents to aid in removing oil films from the surface of the water. The objective of the work was to find spreading agents to reduce the thickness of a burning oil film to the point that it would not sustain combustion or to use these spreading agents to push burning oil away from a ship. The results showed that the agents were incapable of spreading burning oil, although they would spread oil films not on fire. The spreading agents were ineffective against the wind and could not theoretically push back a layer of oil over about one inch thick. Such spreading agents as oleic acid and stearic acid could be used perhaps in calm harbors where the quantity of oil was fairly small and a thick film would not develop.

Literature Cited Concerning Booming

- 1. Ambrose, H. A. Oil Pollution of Seas, Coasts and Harbors, Gulf Research and Development Company Report No. 700R7001. September 1967.
- 2. Sigwalt, R. "The Forces Causing Spreading of Petroleum Products on Water and Their Neutralization by Fatty Oils," Compte Rend, 259(3), pp. 561-64. July 20, 1964.
- 3. Zisman, W. A. and L. Pickett. Wetting and Spreading Agents for Clearing Water Surfaces of Oil Films, NRL P-1930. September 1942.
- 4. "Clearing-up the Oil," Petroleum, p. 95. May/June 1967.
- 5. Dudley, B. L. Harbourmaster's Visit to Cornwall to Study Anti-Oil Pollution Measures, Milford Haven Conservancy Board. April 25, 1967.
- 6. Douma, J. H. Control of Oil Spillage by Booms. Report of the Hydraulic Design Branch Office, Corps of Engineers. August 3, 1967.
- 7. Beynon, L. R. The TORREY CANYON Incident. September 1967.
- 8. The TORREY CANYON. Report presented to Parliament by the Secretary of State for the Home Department by Command of Her Majesty. London, Cmnd., 3246. April 1967.
- 9. Glude, J. F. and J. A. Peters. Recommendations for Handling Gil Spills Similar to that from the Tanker TORREY CANYON. June 1967.
- 10. Anonymous. Skandinavisk Oljeservice AB.

4.6 BURNING

4. 6. 1 Burning at Sea

If a ship or its cargo cannot be salvaged after a stranding, and if a large spill is imminent, possibly the most desirable method of control will be destruction by burning. Preferably this should be done while the oil is still contained aboard ship. Once oil is on the sea, burning becomes increasingly more difficult due to evaporation of the more volatile components, rapid heat transfer to the water (decreasing the oil temperature to below the flash point), and to the lack of oxygen supply to all but the edges of the slick.

Following the stranding of the TORREY CANYON and after salvage attempts had failed, attempts were made to ignite the oil slicks surrounding the ship and to open the decks of the ship and ignite the oil remaining in the holds. Four unsuccessful attempts were made to ignite small slicks which were believed to be reasonably thick in the waters around the TORREY CANYON. Pyrotechnic devices containing sodium chlorate were employed in these attempts with no sign of ignition of the oil.

With regard to burning the oil aboard ship, heavy oils and crudes tend to burn very slowly if the cargo tanks are not opened to the atmosphere. A tanker fire in the Persian Gulf burned for over two months, after which one half of the cargo remained plus an obnoxious residue. (1)

In the case of the TORREY CANYON, estimates place the amount of oil destroyed by burning in situ at between 40,000 and 50,000 gal (British), or over one third of the cargo. (3)

The fire had to be reignited several times. Beynon⁽²⁾ estimated that in the three days of attacks ..."160,000 lb of high explosives, 10,000 gal. of aviation kerosene, 3000 gal. of napalm and several rockets had been dropped on the ship." It is pointed out that several of the bombs failed to detonate and will continue to present a hazard in the area. ⁽¹⁾

In summary, we concluded that destruction of the oil by burning can only be achieved before it is discharged to the sea. Development of improved demolition devices for opening the tanker deck to expose the cargo should be explored.

4, 6, 2 Burning Oil Washed Ashore

The oil coming ashore from the TORREY CANYON proved to be very hard, if not impossible, to burn in most situations where it was tried. (4, 7, 8) Some success was reported in burning where there were pools of unemulsified oil between rocks. (8) Beynon noted: "In places, black oil was present on rocks and in pools between rocks. The pools were sometimes of meat! oil and sometimes of oil floating on water. It was possible to ignue these pools by flame gunning, but an equally successful and more convenient method was to pour a little flame-thrower fuel into a pool, mix it a little with the oil, and then apply a lighted match. Pools of heaf oil burned virtually to completion, but oil burning on water eventually generated enough steam to extinguish the flame and the fire had to be re-ignited on several occasions after first allowing the water to cool. Brown oil in pools only burned so long as the flame-thrower was present and this applied also to the chocolate mousse on the beaches. Even when an 'oxygen tile' was used to effect ignition and wood shavings were mixed with the oil, combustion could not be maintained. It was possible during these tests to watch water boiling out of the 'chocolate mousse' but they effected little beyond producing a thin black skin on the surface. An attempt was also made to burn 'chocolate mousse' by spreading magnesium powder on it and igniting by means of a high temperature flare. This was spectacular but equally as ineffective as using flame-thrower fuel."

The description of a small portable incinerator which was effective in disposing of contaminated debris on the beaches of Cornwall is described in Reference 5. It consists of a 40 gal, open-topped steel drum into which a compressed air line enters tangentially and sloping downward near the top. This air path forms a cyclone on top of the material and the low pressure region near the center tends to hold the flome in a ntac, with the fuel.

Literature Cited Concerning Burning

- 1. The TORREY CANYON, report presented to Parliament by the Secretary of State for the Home Department by Command of Her Majesty. London, Cmnd 3246. April 1967.
- 2. Beynon, L. R. The TORREY CANYON Incident. September 1967.
- 3. Smith, J. W. The TORREY CANYON Disaster. Paper given to Annual Meeting of British Association for the Advancement of Science, Leeds, England. September 6, 1967.
- 4. Oil Clearance, Ministry of Housing and Local Government, MHLG/SWRO/5, Technical Supplement No. 4. April 7, 1967.
- 5. Linsell, R F. Disposal of Waste Oil and Solid Hydrocarbons Contaminated with Sand. Esso Petroleum Company. March 29, 1967.
- 6. The Removal of Oil from Contaminated Beaches. Report prepared for I. M. C. O. by the Warren Springs Laboratory. Report number RR/ES/39. April 1963.
- 7. Dudley, B. L. Milford Haven Conservancy Board Harbour Masters' Visit to Cornwall to Study Anti Oil Pollution Measures. April 25, 1967.
- 8. TORREY CANYON. Detailed Report by Irish Study Team. April 17, 1967.

4.7 SKIMMING

Several mechanical devices are presently being routinely used to remove surface oil from calm water in harbors and waterways. The working principles differ according to usage but generally incorporate either rotating drums, suction devices, or weirs. Several of these devices are self-propelled recovery barges that can traverse a slick until the oil film is picked up.

An example of the rotating drum principal is the M/V PORT SERVICE an oil recovery barge used in the harbor of Baltimore, Maryland. (1) The vessel incorporates the Earle system for oil recovery, which is based upon oil adhering to a rotating drum. (10) Because oil and water are relatively immiscible, only the oil adheres to the drum and is removed by a wiper blade. The system is similar to that used in offset printing: it relies upon the adhesion, cohesion, viscosity, and surface tension of oils and their repulsion to water. The device is relatively insensitive to wave action. The PORT SERVICE is designed for recovery of persistent oils and has an overall length of 38 1/2 ft and displacement of 41.2 tons. It uses four rotating drums. Oil storage capacity is about 3000 gal, and the recovery rate, based on a film thickness of 0,010 in, and a temperature of 70 °F, is about 1000 gal, of 95% pure oil per hour of an average grade Bunker C oil. The high oil to water recovery ratio (about 9 to 1) eliminates the need to discharge the entrained water overboard.

It seems likely that the oil recovery rate of such a system could be improved by applying a hydrophobic plastic foam "sock" or sleeve to the primary oil rotary pickup drum. A "wringer" roller would squeeze the recovered oil from the primary drum.

An example of a recovery barge incorporating the weir principle for oil recovery is the U.S. Navy's Norfolk Naval Shipyard SKIMMER. (2)

An adjustable weir mounted on the forward end is set to induce the surface oil to flow into a sump from where it is pumped into gravity decanting tanks with large holes on the bettom to allow passage of the water out following separation. Recovery is approximately 500 gal. thr under optimum conditions.

The oil is pumped from the sump to the separation tanks by a 65,000 gal. /hr pump. It is estimated that the barge will recover 80% of the oil while traversing a slick.

Another recovery barge, the WATERWISSER, that incorporates the weir principle has been developed by Shell Chemicals in Holland for recovery of oil in harbors and waterways. (3) Oil is skimmed from the surface of the water by means of a moving barge having rigid floating booms hinged on both sides of the barge. These booms open automatically when the barge moves forward. All floating oil entering between the booms will collect where the boom hinges to the barge. From this position it is sucked into the barge through a vertical slot extending below the water surface. In the hold the oil-water mixture is separated by decanting and the oil is stored. The oil-free water is then pumped overboard. The WATERWISSER has a storage capacity of 20 tons and a pumping capacity of 100 tons/hr. The water pump can also be used for pumping oil to shore or into another vessel.

Examples of recovery barges using suction devices are the skimmers used in the Port of Rotterdam for the past 8 years. (4) The oil is picked up from the water with a pump-driven suction apparatus and is pumped to a settling barge. The water which settles out is automatically siphoned overboard. Sizes of this type of craft run from 50 to 200 tons, and the vessels may be self-propelled. The average oil recovery rate is a few tons per hour. Esso Petroleum has an oil recovery barge, the ESSO RECOVERY, at the marine terminal of the Fawley Refinery. (5) It is equipped with a "Victory" oily-water separator and four suction skimmers. Capacity is 30 tons/hr.

All of the present. It is a have, at best, a capacity of a few tons per hour under ideal conditions. The efficiency of all types falls off rather rapidly with increasing wave height, although the rotating drum device probably suffers the least loss of efficiency when compared to the others. Smith (6) states, "Unfortunately no one has yet invented a suction device which works satisfactorily with waves much over 6 in. in height. The problem is that either the device sinks through the oil layer into the water and so sucks

up very largely water, or at the wave trough it is out of the water and sucks air. With some types of pump sucking air loses vacuum and so pumping stops; using other types, sucking air down a fairly long pipe-line inevitably gives some run back and the whole pumping procedure is very difficult. Digging into the water also increases the amount of water which has to be put through the pumps into an oil/water separator and increases the size of the system. As soon as the oil had gotten away from the TORREY CANYON, as indicated above, it was in a very thin layer, and it would have been quite impossible to sweep this layer and suck the oil off the surface. At present there is no suction device which is suitable for use under open sea conditions, though this is a topic on which research might well be undertaken."

Taylor (7) points out the inherent disadvantages of any skimming arrangement:

- (1) "Oil films are usually so thin that large quantities of water are inevitably drawn off also, requiring settling capacity for further oil/water separation. The most sensitive adjusting devices for the skimmer are still incapable of preventing excessive air or water carry-over."
- (2) "When anything but a flat calm prevails, the efficiency of the system falls away rapidly, for obvious reasons."

He goes on to point out the difficulties associated with conventional pumping techniques:

- (i) "To prevent 'gassing,' the pump suction needs to be immersed beneath the liquid surface. A free spiral vortex forms in the nozzle, which results in shearing of the oil film. Thus, after the initial surge, oil ceases to be drawn to the nozzle, a small patch of water is cleared, and, thereafter, nothing but water is pumped off until the nozzle is re-located,"
- (2) "The suction nozzle has to be supported at the appropriate level by appropriate buoyancy. The inertia of such buoyancy arrangements results in the motion of the suction nozzle being out of phase with the wave frequency."

(3) Heavy asphaltic fuel oils when agitated with salt water form very viscous and adhesive water-in-oil emulsions of specific gravity greater than the original oil, but still less than water. Subsequent oxidation further increaser iscosity. Consequently, heavy fuel oil does not spread in films of ever decreasing thickness, as a lighter oil, but floats on the surface in the form of a thick 'tacky' grease which rapidly chokes any suction pipe."

"In order to overcome some of these difficulties, two new methods have been devised at Fawley. For lifting crude oil and lighter oils, an air lift system has been evolved, and, for the heavy fuel oils, a robust rotating cylinder and scraper knife. Neither of these methods has yet been successfully used on a large scale."

The air lift system described by Taylor used a suction nozzle located above the surface of the water. The ejector is air operated and maintains a slight vacuum of 12 in. of mercury in the primary cyclone separator. Air is induced to flow through the open end of the suction hose, which is attached to a nozzle supported on floats about 1 in. above the water. Some of the oil-water mixture is entrained into the tangential inlet of the cyclone separator from which it drains into a secondary gravity separation tank. The oil displaces the separated water out the bottom of the secondary tank. Experiments led to use of a bell-mouth nozzle suspended 3/4 in, above the water surface and corrugated suction hose. Because an ejector with high flow/low vacuum characteristics was desired, the ejector design was based upon the principles of the Coanda nozzle. This device works well only in relatively calm water.

A proposed system to remove surface oil at a high rate would utilize a receiving vessel equipped with several Univac type suction pumps. (8) The larger versions of these pumps, manufactured by Henry Skyes, Ltd. in London, are capable of pumping mixed water and oil at 50,000 gal. /hr or more. A vessel equipped with six such pumps and pumping a mixture containing only 10% oil would recover 7500 gal. of oil per hour. Gravity separation would separate the oil and water and the water would be pumped overboard with a suction pump.

Univac pumps have characteristics that make them appealing for use with standoff vessels. They can operate with suction branches intermittently exposed to air, and with suction lines of up to 400 yards long. This could provide adequate standoff from a vessel that had gone aground on a rocky coast.

Another system for removing oil from the surface of the water has been developed by Dunlop Dracones Consortium. This system employs the Dracone barge, a flexible, towable container for bulk liquid transport by sea. When empty, the barges can be rolled up and stored on the deck of a vessel. A suction device operated by a pump would be mounted on the inlet and a discharge nozzle weighted on the base inside would allow the gravity separated water to flow out when the oil displaced it. The barges are up to 300 ft long, and thus, efficient separation can be achieved by gravity. Tests show that with as little as 5% oil, the final separation is up to 90% effective. When full, the barges would hold up to 1,000 tons and could be set adrift until a convenient pickup could be arranged.

In summary, the possibility exists that a greatly improved skimming vessel could be designed based on incorporation of several of the techniques previously mentioned. For example, the relative wave tolerance but low capacity of the Earle system could be combined with hydrophobic plastic foam "socks" (discussed in Section 4.2.1). The increased oil processing ability would then permit adoption of the WATERWISSER floating boom technique to increase rate of coverage.

Literature Cited Concerning Skimming

- 1. Kabernagel, A. W. "Oil Pollution," U.S. Naval Institute Proceedings. March 1966,
- 2. "Removing Hazardous Oil Slicks at Norfolk," <u>Buships Journal</u>, vol. 5, pp. 39-41. August 1956.
- 3. Milford Haven Conservacy Board. Harbourmaster's Visit to Cornwall to Study Anti-Oil Pollution Measures. April 25, 1967.
- 4. Anonymous. "Removing Oil Spills from Harbours," <u>Docks and Harbour</u> Authority, vol. 43, p. 154. September 1962,
- 5. Anonymous. "Esso Petroleum Company Acts on Oil Pollution," Esso Marine News, pp. 6-7. Summer 1967.
- 6. Smith, J. W. "The TORREY CANYON Disaster," Paper given to annual meeting of British Association for the Advancement of Science. September 6, 1967.
- 7. Taylor, J. C. "The Recovery and Containing of Oil Spills," <u>Journal of the Institute of Petroleum</u>, vol. 40, no. 467, pp. 355-364. November 1962.
- 8. Anony mous. "Clearing-up the Oil," Petroleum, p. 95. May/June 1967.
- 9. "Separating Oil from Water," Engineering. April 28, 1967.
- "The Earle System for Oil Slick Removal," <u>The Navy Civil Engineer</u>, vol. 3, no. 8. August 1962.

4.8 TREATMENT AND DISPOSAL OF RECOVERED SLICKS

4, 8, 1 Introduction

Basically, two general modes of attack are employed in dealing with major oil spills. The first approach is to disperse the oil slick in the open sea or disperse it into the sea after it has been deposited on the shoreface. The second approach is to collect the oil either at sea or after it has been deposited on beaches. In the second case, the problem still exists of disposing of the recovered residue. Since the potentially adverse effects of dispersal techniques are recognized (Section 6.0), it is apparent that, from the viewpoint of the adverse alterations of the marine environment, collection techniques may be preferred. Hence, the question of disposal of recovered oil must receive serious consideration.

The techniques which presently can be employed to deal with recovered oil are those which are now employed in the treatment of refinery wastes. The most extensive source of information in this regard is the "Manual on Disposal of Refinery Wastes," published by the American Petroleum Institute. (1) Most of the basic unit processes discussed in this Manual can effectively be employed to treat the recovered oil-water or oil-water-soil mixtures. For the most part, other methods cited in the literature are variations or combinations of these unit processes.

4.8.2 Oil Recovery

Obviously the best means for disposing of recovered oil is to reprocess the oil subsequent to removal of the water or soil. (1) In many cases, however, such action cannot be taken for economic or logistic reasons or simply due to the difficulty in removing either the water or soil. The following discussion cites processes which can be employed to separate the various constituents so that at least some of the oil fraction can be reprocessed.

Gravity Separation

The first step which is commonly employed in separating oil-water mixtures is gravity separation. (5, 8, 13, 24) A separator developed by the American Petroleum Institute, commonly known as the API separator, is widely used in the petroleum industry. The API separator is used to

BATTELLE NORTHWEST

separate the three principal phases encountered in petroleum wastewater--water, oil, and solids. The API separator design is employed in numerous installations. (21, 36, 38, 45)

The principles of separation are rather basic: large suspended solids settle and accumulate as a sludge, the oil floats to the surface of the separator and is removed by a skimming device, while the aqueous phase is usually routed to further treatment stages. This additional treatment is required since the finer solids are not removed, and some oil will still be present in the effluent from the API separator.

Many attempts have been made to improve gravity separation through designs which either supplement the API design or through innovations. Shell Oil Company in the Netherlands has employed two designs which are claimed to be more efficient than the API design. (31) The designs are modifications of the Shell parallel plate interceptor in which the plane orientation of the plates was found to be critical to efficient oil removal. Kirby (31) makes a point which is critical to all gravity-type separators; that is, the separators are not effective in removing stably emulsified oils.

The National Castings Company has developed an oil-water separator in which the separation is achieved partly by gravity and partly by use of a number of spools of a coalescing medium that forms a semi-permeable wall. (10)

Humble Oil has improved separation efficiencies by the addition of new inlet walls, a center dividing wall, and other hydraulic modifications. (18) Brunsmann reports that the installation of parallel plates in an oil separator also improves efficiency. The plates function as collecting surfaces for oil globules and thus shorten the paths necessary to reach a collecting surface. Up to 60% greater oil removals are reported when compared to a similarly-sized API separator.

Many references cite the use of skimming devices in gravity separation. One such reference $^{(17)}$ describes skimming drums which are installed at entrances to the primary separators. As the water discharges into the separator, the rotary drum skimmer removes oil that has collected at the water surface. The oil recovery rate is from 1.5 to 6 gal./min. Oil

collected in this manner can be reprocessed without further treatment for water removal. A paper by Word describes a somewhat similar system.

Skimming techniques have also been employed to remove oil from open water surfaces. (4) The skimming technique uses one or more floating suction devices. After a series of on-board stages, the recovered oil can be moved as fuel oil subsequent to storage in tanks which allows for additional gravity separation to take place.

In summary, the method most often employed in the primary treatment of oil-water mixtures is gravity separation. The most common device used is the API separator. Improvements which have been suggested are those which modify the skimming or oil collection system by improved skimmers, addition of baffles or parallel plates with varying inclinations, or hydraulic based improvements. In most cases, the collected oil is then reprocessed for further use.

Coagulation-Clarification

As stated previously, the primary stage of treatment--gravity separation--usually is not sufficient in itself to allow discharge of the effluent to the environment. Consequently, a secondary stage is required. This second stage is loosely termed coagulation-clarification. While oil recovered in the primary stage is usually suitable for reprocessing, recovered oil from secondary stage treatment is less likely to be reprocessed.

Air flotation generally can be classified as a clarification technique, Marathon Oil, among others, uses aeration to polish refinery effluent, (12). In this installation, air bubbles, formed in reaction jet inlets, attach themselves to the finely suspended oil particles in the wastewater. The airentrained oil which floats to the surface is removed by surface skimming. Recycle liquid is pumped at relatively high pressures to a microfilm saturation tank where air is introduced. The pressurized, air-saturated stream is restored to atmospheric pressure and passes to the flotation treatment tank. The microscopic air bubbles alter the specific gravity of the oil particles and speeds separation.

In implementing a three year program to modernize wastewater treatment facilities at the Standard Oil (Ohio), Toledo refinery, an air

flotation unit will be built to improve oil removal. (15) Simonsen (44) also reports the benefits of air flotation as a secondary treatment step. Optimum results were obtained when air flotation was used subsequent to chemical flocculation. Less than 10 ppm of oil was evident in the final effluent. Stormont (45, 46) also cites the use of air flotation and its benefits.

Although air flotation has been employed as the sole method of secondary treatment in several instances, usually it is more often preceded by a coagulation or chemical flocculation step. The coagulation step, however, is quite frequently used without subsequent air flotation. The "Manual on Disposal of Refinery Wastes" (1) classifies the coagulation-clarification step as being comprised of the following sequential unit operations: coagulation, flocculation, sedimentation, flotation, and possibly filtration where required. The most commonly added chemicals in the coagulation step are alum and ferric salts. Lime is also added when there is insufficient alkalinity in the wastewater to promote the precipitation of the hydrous oxides. Neuman (38) noted alum and activated silica lead to a highly efficient clarification system. Sadow (42) also cites the efficiency of coagulation-clarification at a large petrochemical plant.

Van Wyk (47) reports an applicat an of coagulation in which aeration is employed to float the flocculant chemical-oil matrix. An example of coagulation-clarification at an American Oil Company Salt Lake refinery has also been reported. (13)

Another method for clarification is that of coalescence. Effectively the process of coalescence occurs when discrete oil globules are encouraged to grow in size by aggregation when promoted by a coalescing medium. A system developed by Kingsbury (30) uses this phenomenon to treat water ballast discharges from fuel tanks. This method utilizes a capacitance probe to detect oil concentrations as low as 1%. When concentrations are detected in excess of this amount, the oil is retained in a slop tank. For the lower concentrations, a two-stage separator is used in which much of the oil coalesces after passage through Dutch weave screens (first stage), and the remainder coalesces in fiber-glass layers (second stage). This system can meet the international standard of 100 mg/liter maximum oil concentration in ship discharges. An example of the application of coalescence is reported for the Baytown Folinery of the

Humble Oil and Refining Company. (16) After the oil has coalesced, the residual wastewater is then filtered.

事を思してみていたが、後に、小さっていることをある。 (日) ボスルース (中) もっているもの (アンション・アン・アン・アン・アンション・アンション・アン・アン・アンション・アンション・アン・アン・アン・アン・アンのの

Filtration through sand filters is presently practiced at a large Russian oil refining plant. (39) Many other filtration methods have been reported. (1) Hay filters are regarded as a rather expedient method of secondary treatment. Two functions are performed by this method. First, it acts as a filter medium and second, the hay will absorb oil. The hay filter has a low absorptive capacity, and because the oil breaks through the filter rapidly, this method is not widely used. Other methods of filtration are preferred to hay filtration. Where oil concentrations are low, vacuum precoat filters have been used with success.

A Russian article cites an example of pressure filtration. (28) A pebble-bed filter has been patented in the United Kingdom. (3) Pebbles of 1/16 in. to 1/8 in. in size were used to filter a wastewater containing 1000 ppm of oil. The effluent from the filter was found to have a concentration of about 20 ppm. To function efficiently, the specific gravity of the oil must be 0.98 or less.

Another process which has been used to clarify or separate oil-water mixtures employs capillary tubes. (40) Oil removal is based on the movement of oil up capillary tubes under pressure. The capillary openings are provided by columns of porous plastic material. The oil passes out at the top of the apparatus and treated water is discharged at the bottom. The apparatus can be cleaned by countercurrent washing with a jet of water.

In summary, most treatment plants which strive for a high degree of efficiency in the secondary stage of treatment of oil-water mixtures employ the following sequence of unit operations. First, alum or ferric salts are added to the wastewater. Lime is added when sufficient alkalinity for precipitation of the iron is not present. The wastewater is then gently agitated or flocculated to promote interparticle collisions for agglomeration. The resultant suspension is then allowed to settle in a sedimentation basin. In some cases where the oil content of the floc is high, flotation is used. This step is followed by filtration through a rapid sand filter or through a multi-media filter.

While the process described above is most often used, coalescence appears to be gaining greater acceptance for similar applications.

4, 8, 3 Bio-Oxidation

Biological treatment of petroleum wastes has been practiced for many years. It is particularly applicable where the oils are low in concentration, i.e., as a polishing step, or where higher concentrations of petroleum constituents in effluents are found to be readily biodegradable. Research has shown that hydrocarbons are biodegradable. However, the rates of degradation are very slow; and, in general, the organisms which metabolize the hydrocarbons do not predominate in the heterogeneous media encountered in the common biological treatment plant. (41,50) On the other hand, ZoBell (50) does point out the "Virtually all kinds of oils are susceptible to microbial oxidation." In addition, Negulescu (37) isolated strains of bacteria which were capable of metabolizing oil in activated sludge. This research was conducted on wastewaters from oil refineries in Rumania. Coe (22) demonstrated that the presence of 25 ppm of oil in refinery wastewater was not detrimental to activated sludge. Ludzack (33) reported on an investigation designed to show the degree of biochemical oxidation of oil under specified conditions.

A variety of biodegradability tests are available from numerous sources. Bunch (20) has recently presented a detailed procedure for determining the biodegradability for all organic compounds. However, the American Oil Chemists' Society standard procedure for the determination of the biodegradability of alkyl benzene sulfonate might be more compatible with procedures for oil degradability determinations. (7)

A water purification program of the Phillips Petroleum Company has demonstrated that the use of biological treatment of refinery wastes after conventional skimming and chemical treatment leads to an efficiency of treatment not feasible with other methods. (11) McKinney (35) has conducted extensive research on biological treatment systems for refinery wastes. Pretreatment by steam stripping is used to reduce hydrogen sulfide levels. Both trickling filters and activated sludge units have been demonstrated to be effective as biological treatment methods. The trickling filters produce good effluents at low loadings, and the activated sludge process is most appropriate where highly purified effluents are required. In both cases surge tanks are required to prevent the detrimental effects

of shock loadings. Oxidation ponds are most effective for treating dilute wastewaters. These ponds are flexible in that they are capable of handling widely varying loads.

Elkin⁽²⁶⁾ reported that biological oxidation of oil refinery wastes in cooling towers represents a highly efficient and economical treatment system. In order to maintain satisfactory quality of recirculating cooling water, high degrees of prior oil removal are necessary. This is accomplished by selective segregation of wastewater at their sources. An extension of this work has reported the experience gained with the reuse system. (36)

Sadow (42) described the efficiency of biological oxidation in mechanically aerated ponds. Wastewater treatment at the Lima refinery of Standard Oil (Ohio) also has been described. (14) A 20-acre pond equipped with floating mechanical aerators provides essentially complete removal of oil, phenols, and other oxygen-consuming materials that would otherwise be discharged.

Stormont (45, 46) has stated that if phenols are present in refinery effluents, biological oxidation or other highly efficient treatment techniques must be used. Sheets (43) reports that biological treatment of phenol can be enhanced by use of temperatures in the thermophilic range, i.e., 52 to 54 °C. He further states that three principal microorganisms are responsible for the destruction of the phenol. Initial seeding with sewage is recommended for bacterial acclimation. Elkin (25) also states that high removal efficiencies of phenols and other organic materials can be accomplished for oil refinery wastewaters especially if properly conditioned prior to treatment. On the other hand. Lynn has shown that the biological treatment process could be operated without sanitary sewage as a seed, thus leading to a more economical and simpler design. Presumably this would be due to a long period for microbial acclimation.

In summary, biological treatment processes--such as activated sludge, trickling filters, aerated ponds, and cooling towers--are highly effective in polishing petroleum type wastewaters. Some disagreement does exist as to the effectiveness of this method to degrade hydrocarbons; however, in light of the fact that this method is commonly regarded as a

third stage of treatment, its function as the last step prior to release to the environment appears highly appropriate.

4.8.4 Sludge Disposal

Sludge disposal is without doubt the most neglected area of the entire treatment scheme. The most generally acceptable method is to dewater the sludge in some fashion and, then, either to incinerate the residue or to use it as fill. (1) Three techniques for dewatering are used. First, the sludge is merely placed in shallow open beds and the water allowed to percolate through the soil. Second, it can be vacuum filtered; and third, it can be centrifuged.

The dewatered sludge can be disposed to a selected ground disposal site or it can be incinerated. (9) Incineration, however, can be rather expensive from a capital and operating costs standpoint. Warner $^{(48)}$ has suggested the use of deep well disposal which could be applicable to dewatered sludge. American Oil Company has scriously considered such an alternative. $^{(6)}$

In the TORREY CANYON incident, it appears that the technique most commonly employed was to dispose of recovered sludges, particularly from beaches, to designated fill or ground disposal sites. The California State Water Pollution Control Board has had experience with oily substances on beaches, but no specific recommendations were made in their report. (2)

An interesting article in the public press has suggested the use of petroleum sludges as mulches in desert areas. (32) The author visualizes spreading the sludges in arid areas to attain a two-fold objective. First, the sludges would have value as mulches, and second, rainfall may be induced if the area covered is large enough.

In summary, techniques for sludge disposal are few. The most common technique employed is to dewater the sludge by gravity drainage in soil, filtration, or centrifugation. The residue is either used as fill or it is incinerated.

4.8.5 Case Studies

It would seem appropriate to cite specific examples of methods which are presently planned or in practice for treating petroleum

wastewaters in order to define the present state-of-the-art. A planned treatment plant for refinery wastewater at the Limb refinery of Standard Oil (Ohio) will incorporate three stages of treatment. $^{(17)}$ The first stage will use gravity separation by the API separator. A chemical flocculationair floatation unit will comprise the second stage, and a mechanically serated pond will be the final step. Easthagen (23) reports a wastewater treatment system which employs the following sequential operations: gravity separation, steam stripping, surge pends, settling pends, sulfide oxidation, chemical oxidation pond, and biological oxidation pond. Hoover (27) described a system which uses gravity separation for removal of free floating oil and settleable solids, lime addition, and air flotation for final separation. A two-channel API separator is used to remove most of the oil from refinery wastewater at Anacortes, Washington. (38) Clarification and additional cil removal are accomplished by two primary clarifiers in which alum and activated silica are used as flocculating agents. The effluent is then treated biologically.

Russian practice at the Novogorkovsk refinery consists of sand separators, a sectional petroleum trap, sedimentation basins, sand filtration, and finally a biological oxidation pond. (39) Wastewater treatment at a large petroleum chemical plant is comprised of skimming followed by coagulation. A mechanically acrated oxidation pond is used for effluent polishing. Stormont reports a treatment scheme which uses API separators for the removal of solid and suspended oil followed by flotation and clarification. Optional biological treatment is employed if high concentrations of phenol are evident.

Literature Cited Concerning Treatment and Disposal of Recovered Slicks

- 1. American Petroleum Institute. Manual on Disposal of Refinery Wastes. Volume I, Waste Water Containing Oil, Seventh Edition. 1963.
- 2. Anonymous. Part I, Quantity of Oily Substances on Beaches and in Nearshore Waters. Part II, Characterization of Coastal Oil Pollution by Submarine Seeps. State Water Pollution Control Board, State of California, Publication No. 21, 1959.
- 3. Anonymous. "Oil Pollution: A Separation Technique," Engineering (Brit.), vol. 193, pp. 445-446. 1962.
- 4. Anonymous. "Removing Oil Spills from Harbours; Development of the I.V. Skimmer," Docks and Harbour, vol. 43, p. 54. September 1962.
- 5. Anonymous. "New Procedures Reduce Ocean Pollution During Tanker Cleaning," World Petroleum. August 1964.
- 6. Anonymous. "American Oil Co. Is Considering (Drilling) Underground Waste Disposal Wells," Petroleum Chem. Engr., 37(5), p. 3. 1965.
- 7. Anonymous. "A Procedure and Standards for the Determination of the Biodegradability of Alkyl Benzene Sulfonate and Linear Alkylate Sulfonate," The Journal of the Am. Oil Chemists' Society, 48(11), November 1965.
- 8. Anonymous. "Humble to Treat Ship's Tank Cleaning," Oil and Gas Jour., 63(9), pp. 78-79. 1965.
- 9. Anonymous. "Incinerator Purifies Plant Effluent," Oil and Gas Jour., 63(37), p. 65. 1965.
- 10. Anonymous. "Oil Separator," Chem. Week, 97(17), p. 130. 1965
- 11. Anonymous. "Phillips Petroleum Co. Has Completed a Water Purification Program," Chem. Week, 96(17), p. 115, 1965.
- 12. Anonymous. "Air Bubbles Polish Refinery Waste Water," Oil and Gas Jour., 64(36), pp. 194-195. 1966.
- 13. Anonymous. "American Oil Co. Adds Water Treating Unit," Oil and Gas Jour., 64(18), p. 148. 1966.
- 14. Anonymous. "Biological Third Stage Treatment," Chem. Eng. News, 44(22), p. 49. 1966.
- 15. Anonymous. "Standard Oil Co. (Ohio) Modernization." Oil and Gas Jour., 64(18), p. 60. 1966.
- Anonymous. "Waste Disposal/How Humble Oil and Refining Co. Combats Water and Air Pollution," Oil and Gas Jour., 64(13), pp. 132-135. 1966.

- 17. Anonymous. "Rotating Drum Removes Oil Film from Water," Chemical Engineering, p. 112, 1967.
- 18. Bozeman, H. C. "Humble Oil and Refining Co. Improves Oil-Water Separation," Oil and Gas Jour., 63(2), pp. 92-93. 1965
- 19. Brunsmann, J. J., J. Cornelissen, and H. Eilers. "Improved Oil Separation in Gravity Separators," J.W.P.C.F., vol. 34, p. 44. January 1962.
- 20. Bunch, R. L. and C. W. Chambers. "A Piodegradability Test for Organic Compounds," Jour. Water Poll. Cont. Fed., vol. 39, p. 181. February 1967.
- 21. Burroughs, L. C., and G. E. Sample, "Pollution Control at Shell Oil Refineries," Sew. and Ind. Wastes, vol. 30, pp. 57-64, 1958
- 22. Coe, R. H. "Bench-Scale Biological Osidation of Refinery Wastes with Activated Sludge," Sewage and Industrial Wastes, 24(6), p. 731. June 1952.
- 23. Easthagen, J. H., V. Skrylov, and A. L. Purvis. "Development of Refinery Wastewater Control at Pascagoula, Mississippi," J.W.P.C.F., vol. 37, p. 1671. December 1965.
- 24. Eaton, C. D., R. R. Evans, and E. G. Komnick, "Reclamation of Refinery Effluents," Ind. and Eng. Chem., vol. 46, p. 319, 1954.
- 25. Elkin, H. F. "Activated Sludge Process Applications to Refinery Effluent Waters," Sewage and Industrial Wastes, 28(9), p. 1122. September 1956.
- Elkin, H. F., E. F. Mohler Jr., and L. R. Kumnick. "Biological Oxidation of Oil Refinery Wastes in Cooling Tower Systems," Sewage and Industrial Wostes, 28(12), pp. 1475-1483. 1956.
- 27. Hoover, W. E., W. D. Sitman, and V. T. Stack. "Treatment of Wastes Containing Emulsified Oits and Greases," Presented at meeting of the American Society of Labricating Engineers, Chicago, Ill. May 1963.
- 28. Karelm, Y. A. and A. G. Sokolov. "Closed System Purification of Waste Waters in Industrial Oil Treatment Plants," Neft. Khoz., 44(5), p. 47. 1966 (Russian).
- 29. Kharitonova, P. "Purification of Ships' Waste Water From Oil Impurities," Eschouy Transport, no. 11. November 1960.
- 30. Kingsbury, A. W. "Development of an Oily Water Separator," J. Water Poll, Con. Fed., 38(2), pp. 236-240, 1966.
- 31. Kirby, A. W. W. "The Separation of Petroleum Oils from Aqueous Effluents," Chem. Engr. Lond. no. 177, p. 76. 1964.

32. Knowles, R. S. "Oil on Troubled Sands," The Rotarian, p. 44. August 1966.

 $P_{E_{i}}^{p_{i}}$.

- 33. Ludzack, F. J. and D. Kinkead. "The Persistence of the Motor Oil Class of Hydrocarbons in Polluted Water Under Aerobic Conditions," Presented at the National ACS Meeting, Cincinnati, Ohio. April 4, 1955.
- 34. Lynn, G. E. and T. J. Powers. "Bacterial Studies in Oxidation of Phenolic Wastes," Sewage and Industrial Wastes, 27(1), p. 61. January 1955.
- 35. McKinney, R. E. "Biological Treatment Systems for Refinery Wastes," Journal of Water Poll. Con. Fed., 39(3), pp. 346-359. March 1967.
- 36. Mohler, E. F., H. F. Elkin, and L. R. Kumnick. "Experience with Reuse and Bio-Oxidation of Refinery Wastewater in Cooling Tower Systems," Journal Water Poll. Con. Fed., 36(11), p. 1380.

 November 1964.
- 37. Negulescu, M., L. Vaicum, and S. Godeanu. "Aspects Concerning the Treatment of Wastewaters Resulting from Oil Refineries in Rumania," Journal Water Poll. Con. Fed., 8(3), pp. 362-363. 1966.
- 38. Neuman, E. D., C. J. Reno, and L. C. Burroughs. "Waste Disposal at Anacortes," Oil and Gas Jour., 56(20), p. 124. 1958.
- 39. Nikolaev, V. M. "Effectiveness of the Purification of Effluents from the Novo-Gorkovsk Oil Refining Plant," Gigiena i San. (USSR), 29(11), p. 85. Chem. Abs., vol. 62, p. 7495. 1965.
- 40. Pontant, M. "The Struggle Against Pollution of Waters by Petroleum Products and Other Oily Substances," Techq. Eau Assain, 15(180), p. 59, 1961.
- 41. Prokop, J. F. "Report on a Study of the Microbial Decomposition of Crude Oil," 81 pp. Mimeo, Texas A&M Research Foundation.
 May 29, 1950.
- 42. Sadow, R. D. "Waste Treatment at a Large Petrochemical Plant," Journal Water Poll. Con. Fed., 38(3), pp. 428-441. 1966.
- 43. Sheets, W. D., M. K. Hamdy, and H. H. Weiser. "Microbiological Studies on the Treatment of Petroleum Refinery Phenolic Wastes," Sewage and Industrial Wastes, 26(7), p. 862, 1954
- 44. Simonsen, R. N. "Oil Removal by Air Flotation at Sohio Refineries," Session on Waste Disposal During the 27th Midyear Meeting of the American Petroleum Institute's Division of Refining, in the Fairmont Hotel, San Francisco, California. May 15, 1962.
- 45. Stormont, D. H. "Report on Waste Disposal Progress/Refiners Join Attack on Water Pollution," Oil and Gas Jour., 64(130), p. 139. 1966.

- 46. Stormont, D. H. "Waste Disposal/Water Conservation California Style," Oil and Gas Jour., 64(13), p. 140. 1966.
- 47. Van Wyk, J. W. "Design for a Portable Waste Treatment Plant for Study of Flocculation," Session on Waste Disposal During the 27th Midyear Meeting of the American Petroleum Institute's Division of Refining, in the Fairmont Hotel, San Francisco, California. May 15, 1962.
- 48. Warner, D. L. "Deep Well Disposal of Industrial Wastes," Chem. Eng., vol. 72, p. 73, 1965.
- 49. Word, J. C., M. V. Wright, and R. W. Klippel. "How Phillips Petroleum Co. Treats Its Complex Wastes at Borger (Texas)," Oil and Gas Jour., 64(12), p. 98. 1966.
- 50. ZoBell, C. E. "The Occurrence, Effects, and Fate of Oil Polluting the Sea," Int. J. Air Wat. Poll., vol. 7, pp. 173-198, 1963.

5.0 RESTORATION

5.0 RESTORATION

5.1 BEACHES

Several approaches have been and can be taken in restoration of beaches heavily contaminated by oil. These methods include

- Extensive application of detergents accompanied by mechanical tilling to expose deeply contaminated sand
- Plowing under or burying contaminated sand
- Physical removal of the contaminated surface layer for inland disposition
- A combination of the above methods.

All these means have been used. Their relative success can only be judged by extensive review of articles appearing in the popular press combined with estimates of effectiveness and costs as judged by those involved in directing restoration activities or those reporting later as observers.

In general, any procedure applying to a sandy beach can be extended to a gravel or shingle beach, but usually with greater difficulty as the aggregate size increases. Similarly, the various restoration procedures are applicable to all navigable waterway shorelines. The method or combination of methods to be applied in any instance must targely be determined on site, based on the availability of equipment and supplies of chemical and physical treating agents and disposal sites for oil contaminated materials.

The use of detergents and emulsifiers has been previously discussed in Section 4.3. As a general statement, restoration by this method in the case of major oil contamination has proved inefficient and resulted in deeper penetration of the oil into the beach sands. This necessitated continued reworking for exposure either to more detergents or to natural washing by the sea.

The oil from the TORREY CANYON that reached the beaches presented an especially difficult problem of disposal in that it had been paratially emulsified at sea. Beynon⁽¹⁾ stated, "In principle it is better to remove oil from a beach rather than to emulsify and disperse it not the sea using detergent and water, and only where physical removal is not practicable should detergent be used. Because the nature of both pollution and

beaches varies greatly from one place to another, it is not possible to recommend any methods which would be universally applicable. The best way to deal with oil pollution in any particular place must be decided on the spot, and the decision is also influenced by what mechanical equipment is available.

"In some instances it is possible to use a bulldozer to skim off a surface layer of sand and oil. This should then be removed from the beach and disposed of, or at least moved above high tide mark for subsequent disposal or incineration. Where oil spots or balls of oil and sand are widely dispersed, the surface sand may be pushed into windrows using wooden squeegees and the windrows bulldozed up and removed. Where such oil spots and balls of oil and sand are left at a tide mark it is often possible, as an alternative, to remove them with shovels or by hand. These methods of physical removal of the oil are usually limited to instances where the oil is on or near to the beach surface. Where an oil/sand mixture is deep, the amount of sand which has to be removed with the oil magnifies the task of physical removal and disposal to impracticable proportions, especially as many beaches need to retain all their available sand. Where an oil layer has not mixed with sand but has become buried under a deep layer of clean sand, it is possible to bulldoze the clean sand away thus exposing the oil and allowing it to be removed as for surface oit; the clean-sand-may-then be bulldozed back into position.

"It has been reported that a considerable degree of success has been achieved in Guernsey and France in removing liquid oil from beaches by use of sewage carts normally used for clearing cesspits. The suction pipe from the vehicle is used to draw the oil into the vehicle tank and the oil is pushed to suction point by means of brooms and wooden squeegees to keep the suction line supplied. The oily waste is thus removed and dumped.

"Even if it is only feasible to remove a portion of the offending oil from a beach by physical means, this should be undertaken to lessen the subsequent task of emulsifying and dispersing it in the sea." The Ministry of Housing and Local Government bulletin "Oil Clear-ance" states, "In principle it is better to shift the oil away from the beach rather than wash it away with detergent, and only where physical removal is not practicable should detergent be used."

Covering the contaminated portion of the beach as means of restoration is wholly unsatisfactory as the oil will eventually reach the surface again as a result of wave action, and little weathering to a less annoying state is possible under sand cover.

To process the contaminated sand or gravel while it is still on the beach invariably involves some process of mechanical working combined with the use of detergents. Dudley (3) observed. "Obviously, in the case of the "TORREY CANYON" the pollution was so severe that methods of cleaning beaches which would appear almost ludicrous in normal circumstances were tried, but it would appear that all successful methods employed the use of detergents in one form or another. I was informed that earth moving equipment, and preferably tracked earth moving equipment, is vital in any large scale operation and I was strongly advised to suggest that Pembrokeshire should consider keeping an up-to-date list of all heavy earth moving equipment in the County so that it could be quickly mobilized if very severe pollution-occurred.—Some authorities suggested to me that with the knowledge they now have they would seriously consider, if something similar happened again, getting in earth moving equipment immediately, and certainly before the bil arrived, to remove the top two, three or even four feet of any important amenity beach and stowing the sand inland until the oil had been cleared and then put the top of the beach back in place."

The majority of the oil from the TORREY CANYON was treated with detergents while at sea so it tended to contaminate a greater portion of the beach and generally penetrated deeper than pure crude or heavy oil would have been expected to do. (4) For sandy beaches in England the treatment generally involved turning the top layer of the sand over mechanically, then spraying with detergents within one hour of the incoming tide and either hosing down or awaiting tidal action. When heavy earth moving equipment

The Ministry of Housing and Local Government bulletin "Oil Clear-ance" states, "In principle it is better to shift the oil away from the beach rather than wash it away with detergent, and only where physical removal is not practicable should detergent be used."

Covering the contaminated portion of the beach as means of restoration is wholly unsatisfactory as the oil will eventually reach the surface again as a result of wave action, and little weathering to a less annoying state is possible under sand cover.

To process the contaminated sand or gravel while it is still on the beach invariably involves some process of mechanical working combined with the use of detergents. Dudley (3) observed. "Obviously, in the case of the "TORREY CANYON" the pollution was so severe that methods of cleaning beaches which would appear almost ludicrous in normal circumstances were tried, but it would appear that all successful methods employed the use of detergents in one form or another. I was informed that earth moving equipment, and preferably tracked earth moving equipment, is vital in any large scale operation and I was strongly advised to suggest that Pembrokeshire should consider keeping an up-to-date list of all heavy earth moving equipment in the County so that it could be quickly mobilized if very severe pollution occurred. Some authorities suggested to me that with the knowledge they now have they would seriously consider, if something similar happened again, getting in earth moving equipment immediately, and certainly before the oil arrived, to remove the top two, three or even four feet of any important amenity beach and stowing the sand inland until the oil had been cleared and then put the top of the beach back in place."

The majority of the oil from the TORREY CANYON was treated with detergents while at sea so it tended to contaminate a greater portion of the beach and generally penetrated deeper than pure crude or heavy oil would have been expected to do. (4) For sandy beaches in England the treatment generally involved turning the top layer of the sand over mechanically, then spraying with detergents within one hour of the incoming tide and either hosing down or awaiting tidal action. When heavy earth moving equipment

shingle into the sea. Again it is essential that a deterged shingle beach should be washed by the sea within an hour of deterging, otherwise the oil may penetrate very deeply into the shingle.

Allowing the oil to come ashore to weather was recommended by Glude following an inspection tour. After weathering on the beach, the oil tends to agglomerate with the sand and is then quite readily recovered by toothed discs dragged behind a tractor along the beach.

Dennis, ⁽⁷⁾ during a one year study of U.S. East Coast beaches, found that oil comes ashore in several distinct forms and graded them from 1 to 6. The classifications were as follows:

- 1. Liquid film covering beach or water surface
- 2. Sticky, very soft, often sand coated
- 3. Nonsticky, putty-like, doesn't crack when worked
- 4. Nonsticky, cracks when worked
- 5. Solid, nonworkable
- 6. Coquina oil, a rather brittle mixture of shells, shell particles, oil, and sometimes sand.

He encountered No. 3 type oil most commonly during the study. He surmizes that oil reaching the beach in a No. 2 condition is fairly fresh, perhaps not more than a few days old, and will eventually form coquina oil (No. 6) if left on a sandy beach.

5.2 ROCKY COASTS, SEAWALLS, AND STRUCTURES

The most commonly used method in England following the TORREY CANYON to clean rocks, where they were accessible, was to apply detergent followed by either vigorous hosing or tidal action. Another satisfactory method was to apply a mixture of high pressure steam and detergent followed by tidal action. (1)

Benyon states, "Oil stained harbour and estuary walls can also be cleaned effectively by spraying with detergent and then hosing down with jets of water. At one site in Cornwall, high pressure steam mixed with detergent was used to clean harbour steps, but such equipment is not generally available. Claims have also been made that oil stained walls can be cleaned by hurning the oil with a high temperature, oxy-propane flame. Because of the justified reluctance of the authorities to use detergent in the Hayle Estuary wild life protection area, this location was chosen to demonstrate the oxy-propane burning method. Several important disadvantages came to light during this demonstration. The necessary equipment included gas cylinders which made it clumsy in use and difficult to transport; it was expensive to use and the rate at which the oil was burned appeared to be far too slow in relation to the vast area of wall which needed cleaning. Although oxy-propane flame left the wall very clean, the high temperature caused the surface of the wall to flake off to a depth of 1/32 to 1/15 inch. Examination of the flakes of wall which fell to the ground showed that the black stain was still present and that the clean appearance of the wall was largely due to the removal of the wall surface rather than to complete combustion of the oil. All in all, this method could not be considered useful except, possibly, in very special circumstances. Burning oil off walls using flame-throwers is also unsatisfactory because of the slowness of the method and the excessive quantity of fuel used.

"As for oil stained walls, the quickest, most efficient and probably the only practicable way of cleaning polluted rocks involves spraying with detergent followed within a few minutes by hosing down with high pressure jets of water. Care must be taken to hose the area thoroughly, otherwise the under-sides of rocks remain polluted and pools of oil/detergent lie in

crevices. If there is a high sea running which will reach the rocks soon after deterging, hosing of the area is unnecessary. In a calm sea, however, the tendency is for the oil to be lifted off the rocks without being dispersed, and to drift away in small slicks probably to pollute or re-pollute another area of the coast. For the reasons given for harbour and estuary walls, as well as the even greater difficulties in application, neither oxy-propane flaming nor the use of flame-throwers is practicable for cleaning rocks."

The French attempted hand scraping and scrubbing the rocks and had only limited success because it was impossible to remove all of the oil between cracks and crevices and the labor requirements were excessive.

Literature Cited Concerning Restoration

- 1. Beynon, L. R. The TORREY CANYON Incident. September 1967.
- 2. Oil Clearance. Report issued by Ministry of Housing and Local Government. MHLG/SWRD/5. April 7, 1967.
- 3. Dudley. Milford Haven Conservacy Board. Harbourmaster's Visit to Cornwall to Study An.i-Oil Pollution Measures. April 25, 1967.
- 4. Glude, J. B. and J. A. Peters. Observations of the Effect of Oil from the Tanker TORREY CANYON and Oil Control Measures on Marine Resources of Cornwall. England and Brittany, France. June 1967.
- 5. Glude, J. B. and J. A. Peters. Recommendations for Handling Oil Spills Similar to that from the Tanker TORREY CANYON. June 1967.
- 6. The Removal of Oil from Contaminated Beaches. Report prepared for I. M. C. O. by Warren Spring Laboratory, Report No. RR/ES/39, April 1963.
- 7. Dennis, J. V. Oil Pollution Survey of the United States Atlantic Coast. May 15, 1959.
- 8. Environmental Sci. Tech., p. 273, April 1967.
- 9. Caldwell, Joseph M. Oil Pollution of the Shore Face Caused by the TORREY CANYON Disaster. August 1, 1967.

5.3 RESTORATION OF WATERFOWL

Floating oil is an abnormal constituent of a bird's habitat, and waterfowl do not appear to have developed any capacity to avoid it or to distinguish polluted from unpolluted areas. That extensive mortalities of birds result from contamination by oil is thoroughly documented in the literature (Section 6.2). The question posed by many individuals and agencies concerned with the problem is whether oiled birds can be cleaned and restored to their original condition.

Brief accounts of cleaning waterfowl that were contaminated with oil are given by Lincoln, (5) Peterson, (8) and Ripley. (9) Recent discussions of the magnitude of the task and the complications involved are provided by Peller, (7) Erickson, (2) Merrin and Jackson, (6) Rook, (10) and The Waterfowl Trust. (1) The physical condition of an oiled bird when finally recovered is very important. Rook (10) believed that if a bird is thoroughly oiled, thin, or weak it should be humanely destroyed; if it is lightly oiled, the bird may have a 20% chance of survival provided it is given proper treatment.

A bird at the time of recovery is probably suffering from exposure to cold, due to loss of protective insulation; from starvation, since it has been unable to feed; and from sickness, since it may have ingested some of the oil. Requirements of the basic treatment include war.nth suitable for a warm-blooded animal, food suitable for the species of bird involved, immediate cleaning of the adhering oil, and a period of rehabilitation prior to release. Treatment is complicated by the inherent wildness of water-fowl, as well as by the pathological conditions associated with the ingestion of toxic oils. (1, 3)

Erickson⁽²⁾ noted that many methods of removing oil and tarry deposits from waterfowl plumage have been attempted. Some solvents used to clean birds cause considerable irritation of the skin. The loss of natural oils from the plumage and the breaking of the interlocking mechanism of the feathers often requires that the birds be retained a week or more in captivity before they can be released. Soap and water usually have little value in removing oil and tar.

Manual procedures used to remove oil from plumage are involved and time consuming. (2, 5, 8, 6, 7, 10) Several ingredients applied singly or in combination include: "dry-shampoos" of Fuller's earth or powdered chalk, butter, margarine, vegetable oils, Neat's-foot oil, oleic acid, commercial detergents, and sulphonated castor oil. Individual attention is necessary for each contaminated bird.

Rook, (10) in the aftermath of the TORREY CANYON, noted the lack of authoritative information on successful methods of cleaning birds. She found that although many people claimed they had been successful in the past, when their methods were examined there were divergent opinion on the methods recommended. Furthermore, no one could say that the birds they cleaned survived more than a day or two when returned to the sea.

Rook (10) summarized the best advice then available on cleaning methods. "If the bird has considerable area of oil on its body, then one can try washing it gently in a mild washing-up detergent, being careful to stroke it in with the lie of the feathers in order not to break them, then wash it out very thoroughly in warm water. The Royai Society of Prevention of Cruelty to Animals has used Saroul (sulphonated castor oil) successfully. The bird must then be wiped gently with rags and dried, preferably with a fan heater such as a hair dryer, then put into a room with a temperature around 70 °F. A bird that is not in too serious condition will then try to preen itself, which is a good sign." Rook then reviewed post-treatments including feeding, maintenance, and exposure to sea water for bathing and swimming.

Observations on rehabilitation of oiled sea birds from the TORREY CANYON, primarily auks, are given by The Waterfowl Trust. (1) Early mortality was heavy and accompanied by hemorrhagic enteritis, suggesting a powerful irritant possibly of the phenolic type. Oedematous skin lesions further suggested toxic action by oil and/or detergents. The kidneys of the birds showed some pathological changes, and respiratory congestion was frequently encountered. Secondary complications following the initial losses included the disease aspergillosis and infective arthritis of the "ankle" joint from prolonged contact of the feet with hard surfaces. Various vitamin suppliments were fed to the birds, but most of the birds eventually perished.

Generally, attempts to clean large numbers of oiled birds--despite the humane merits--are usually futile. The TORREY CANYON disaster emphasizes the point. According to Spencer, (11) one month after the wreck and dispersal of the oil, 7849 birds had been recovered. Of these, 2038 were dead or moribund when delivered to various cleaning stations. Although over 5800 birds were cleaned, only 500 (8.6%) remained alive at the time of Spencer's report, and the total surviving decreased week by week.

Erickson⁽²⁾ noted that, "Unfortunately, by the time that contaminated birds can be captured, many, if not all of them, are beyond assistance because of external injury, toxic effects, exposure, or starvation. It is not economically feasible to patrol, with sufficient frequency and thoroughness to pick up contaminated birds in time to save them, all the vast expanses where migratory birds may encounter oil. Also, the decontamination and rehabilitation processes fow in use are rather laborious and time comsuming, so that the costs of treatment remain high." Obviously, consideration of large-scale operations to rescue oiled birds must recognize that, in all probability, only a few of the birds will be recovered. Many birds die at sea and are in moribund condition if they are able to reach shore. Contamination of many populations by oil occurs in inaccessable areas and are never reported. Furthermore, as noted by Hawkes. (4) mortalities occurring over a long period of time from relatively minor spills or releases of oil may exceed the losses occurring from the spectacular accidents.

The most satisfactory solution to saving birds from oil pollution is for those concerned with conservation and amenity to continually press for safeguards against the intentional release of oil, and to find more effective techniques for dealing with accidental spills.

Literature Cited Concerning Restoration of Waterfowl

- 1. Anonymous. The Attempted Rehabilitation of Oiled Sea Birds at Slimbridge, April-July 1967. Interim Report (unpublished mimeo), The Waterfowi Trust, Slimbridge, England, 9 pp. 1967.
- 2. Erickson, R. C. "Effects of Oil Pollution and Migratory Birds."

 Biological Problems in Water Pollution, 3rd Seminar, 1962,
 R. A. Taft, San. Eng. Cent., Cincinnati, Ohio, pp. 177-181, 1962.
- 3. Hartung, R. and G. S. Hunt. "Toxicity of Some Cils to Watertowi," J. Wildlife Mgt., 30(3), pp. 564-570, 1966.
- 4. Hawkes, A. L. "A Review of the Nature and Extent of Damage Caused by Cil Pollution at Sca," <u>Trans. 26th N. Amer. Wildlife Conf.</u>, pp. 342-355. 1961.
- 5. Lincoln, F. C. Treatment of Oil-Soaked Birds, Wildlife Leaflet No. 221, U. S. Fish and Wildlife Service, 2 pp. 1942.
- 6. Merrin, P. and B. S. Jackson. "R. S. P. B. Action," <u>TORREY CANYON Birds</u>, 1(10), pp. 201-212, 1967.
- 7. Peller, E. 'Operation Duck Rescue (Minnesota), Audubon, 65(6), pp. 364-367. 1963.
- 8. Peterson, R. T. "Birds and Floating Oil," Audubon, 44(4), pp. 217-225, 1942.
- 9. Ripley, D. "Oil on the Sea," Audubon, 44(2), pp. 86-90. 1942.
- Rook, D. "To Clean or Kill?," <u>TORREY CANYON Birds</u>, 1(10), pp. 201-212. 1967.
- 11. Spencer, R. "The Effect on Birds," TORREY CANYON Birds, 1(10) pp. 201-212, 1967.

6.0 BIOLOGICAL AND ECOLOGICAL EFFECTS

6.0 BIOLOGICAL AND ECOLOGICAL EFFECTS

6.1 OIL POLLUTION AND FISH AND SHELLFISH

Introduction

The possible results to the biota from spills of oil and oil products and the detergents and emulsifiers used in the subsequent cleanup procedures are of concern to those who use the plants and animals on these shores and beaches as a source of recreation and sport and commercial fishing. There are a prodigious number of reports in the literature concerning the effects of oil, oil products, and detergents on marine and freshwater molluses, crustaceans, and fish. However, many of these accounts lack quantitative information and are often based on sentiment and superficial observation. These reports (6, 123, and others) do, however, serve a purpose in developing public awareness of the potentially pernicious effects that may result from oil pollution. On the other hand, the reports with scientifically valid data have dealt mainly with what levels of oil, oil products, and detergents that are lethal to the animals under study.

Death in an animal is usually easy to determine, and for this reason has been used as the criterion for determining whether or not the various pollutants are harmful. However, there are certain animals in which the time of death is difficult to evaluate, such as some shellfish. (127) Nevertheless, very few investigators have studied the chronic effects that may arise from sublethal levels of pollution with oil or detergents, such as impaired physiology, genetic aberrations, sterility, and carcinogenesis. Butler, et al. (10, 11) found that sublethal doses of pesticides impaired the physiology of oysters, and Hueper (45) showed that petroleum and derivatives were possibly responsible for neoplasms in marine animals. Therefore, these are important aspects that should be studied before any categorical statements can be made concerning the effects of these pollutants upon fish and shellfish.

The literature covered in this section of the review is extensive, but should not be considered as complete. However, the major and most pertinent references have all been covered in this review section. This

section is divided into two major areas. The effects on (1) fish and (2) shellfish. The effects of oil, oil by products and derivatives, and detergents will be considered separately under each of the two major headings.

Fish

Several review articles deal with the effects of oil, oil products, and detergents on fish. (2, 3, 4, 5, 43, 45, 82, 110, 111, 112, 150) Each year the United States Public Health Service gives a listing of the fish kills in the United States caused by pollution, and in their 1964 report, (5) kills attributed to oil pollution ranked high on the list on both number of incidents and the number of individual fish killed. Gregg (41) briefly reviews the various causes of fish mortalities and lists the pathological symptoms caused by various common toxicants. Reichenback-Kline (106) has given a detailed account of the general reactions of fish to pollutants. Under conditions of slight pollution, there is a decline in the populations of fish, and as the pollution progressively increases, the fauna declines through a graded series to major fish kills and the complete disappearance of the various fish species.

Crude Petroleum. There are very few factual reports on the effect of crude oil on fish, and there is some difference of opinion as to the exact nature and variety of the effects of oil on different species of fish. ZoBell (150) states that only at its worst does oil pollution appear to be injurious to animals in the sea. In general, there are five principal ways in which oil may affect marine animals, according to Hawkes. (42) These are the tainting of the flesh of fish and shellfish, thus rendering them inedible; poisoning of the animals by ingestion of oil or its soluble fractions; disturbance of food chains; physical fouling of animals with heavy coats of oil; and repellent effects.

The devastating effect produced by releasing 10,000 tons of crude oil on the shore of Guanica, Puerto Rico, was described by Diaz-Piferrer. (20) The author had maintained an algae collection station at this site for an entire year prior to the disaster and was therefore able to readily evaluate the effects of the oil spill. The damage was extensive and a variety of fish, particularly clupeoids, were found dead in the area.

The deleterious effect of crude oil and lubricating oils on fish is due to a film formed over the gill filaments of fish, preventing the exchange of gases and resulting in anoxia and suffocation. (54, 144) Experimental results by Wiebe (144) corroborated these observations using several species of fish; bass, bream, crappie, and sunfish. It was noted that the size of the fish is very important in determining the toxicity of the crude oil. The larger fish were more resistant to the effects of the oil. A breakdown of capillaries and accompanying hemorrhage in the caudal fin, which resulted in sloughing of parts of the fin, was noted by Wunder (146) as a characteristic lesion of oil pollution effects on young carp.

Oil Products and Derivatives. The effects of oil refinery effluents have been studied on a variety of fish. (8, 22, 23, 38, 40, 51, 52, 102, 128, 137, 143, 145)

Wallen (145) determined the safe tolerance levels of various refinery wastes to the mosquitofish. Gambusia affinis, in fresh water (Table 6.1-1). He concluded that there is little chance that these substances would be present in natural waters in harmful concentrations. Sugimoto, et al. (128) found that fish damage due to oil pollution was intensified by the rapid development of the oil industry and the subsequent discharge of oil refinery wastes. It was found that crude oil discharge from a Seto Inland Sea refinery varied from 0,09 to 4 tons of oil per day. Most investigators feel that refinery effluents have a deleterious effect upon fish, but that it may be related to seasons, (8, 64) dilution of effluent, (40) pH, (52) the metabolic rates of the individual fish, and the various ambient environmental conditions. (51) The median tolerance limits of a variety of fish has been shown in three papers. (23, 51, 143) The most toxic constituents of oil refinery effluents were found to be ammonia, phenol, and sulphide. The toxicity of ammonia increased and that of sulphide decreased with increase in pH value, while the toxicity of phenol was unaffected by the pH. (52) The tolerance of goldfish of various ages to phenol was reported by Lukyanenko and Flevor, (63) and they noticed a decreased tolerance with age up to 12 months. These same authors (64) studied the seasonal resistance of carp to phenol. They found a higher mortality in summer than in winter, which was attributed

to the high metabolic rate of fish in summer. The relative resistance of several fish to various petrochemicals, such as phenols, cresols, and naphthalene has been studied by numerous investigators, all of whom agree that these are highly toxic to fish. (49, 55, 57, 62, 76, 79, 103, 116, 118, 125, 131, 138) Holland, et al. (49) found naphthalene and phenols were highly toxic to silver salmon and rainbow trout and caused complete mortalities in less than 9 hr in 5. 6 ppm of naphthalene and distress in 17 min in 5.6 ppm of phenols. Tagatz (133) conducted experiments on juvenile American shad, Alosa sapidissima, to determine the toxicity of petroleum products and of petroleum products with accompanying low dissolved oxygen. Median tolerance limits (TL_m) were determined for gasoline, diesel fuel oil, and bunker oil. Gasoline was the most toxic, fuel oil somewhat less toxic, and bunker oil the least toxic (Tables 6.1-2 and 6.1-3). A synergistic relation appears to exist between the combined effects of low oxygen and oil pollution that increases their toxicity to fish. Oil concentrations that are tolerable to fish when accompanied by high oxygen levels probably become lethal when oxygen is just adequate for fish survival. Petroleum product concentrations that were tolerable to juvenile shad when accompanied by dissolved oxygen greater than 6.0 ppm were lethal at oxygen levels ranging from 1.9 to 3.2 ppm.

TABLE 6.1-1. Median Toxicities and Safe Concentrations for Organic Compounds Toward Mosquitofish(145)

Co	inpounds Toward Mosquitonsin- A			Sale		
	Median Toxic Limit, ppm			Concentrations, ppm		
Substance	24-Hr	48-Hr	96-Hr	48-Hr	96-Hr	
Furtural	44	24	24	2.1	7	
n-Amyl acetate	65	65	65	19	19	
Phenol	72	72	72	21	21	
Naphthalene	220	165	150	27	37	
Acetic acid	251	251	251	75	75	
4-Amino-m-toluen sulfonic acid	e- 425	410	375	111	94	
Benzene	395	395	386	118	110	
Pyridine	1,350	1,350	1,300	405	361	
Diethanolamine	2, 310	2,310	1, 990	693	443	
2-Putanone	4,508	4, 508	4,50 8	1, 352	1,352	
Heptane	4,924	4, 924	4, 924	1, 468	1, 468	
Diethylene glycol	>10,000	>10,000	>10,000	3, 000	>3, 000	
Acetone	13,500	13,000	13,000	2, 845	3, 073	
Acetamide	15, 500	15, 500	15,500	4, 650	4,650	
Cyclohexane	15, 500	15, 500	15,500	4, մ5 0	4, 650	

TABLE 6.1-2. Survival of Juvenile American Shad, Alosa Sapidissima, Subjected to Different Concentrations of Petroleum Products for Specified Time Intervals (133)

	Concentration	Number	surviving	r after ^(a)
Petroleum product	mg/liter	24 hr	48 hr	96 hr
Gasoline	152	U	0	
	114	0	0	
	99	2	2	
	84	8	8	
	68	10	10	
	38	10	10	
Diesel fuel oil	334	2	2	
	251	3	2	
	167	7	5	
	1 25	8	7	
	84	10	9	
Bunker oil	2, 417	3	5	2
	1,952	10	8	5
	1,580	10	9	7
	1,302	_ 1.0	10	10
	837	10	9	9
	372	10	10	10

⁽a) Ten fish used in each test.

TABLE 6.1-3. TLm (Median Tolerance Limit) Values of Gasoline, Diesel Fuel Oil, and Bunkey Oil for Juvenile American Shad, Alosa Sapidissima

	TL _m (mg/liter)				
Petroleum product	24 hr	18 hr	96 hr		
Gasoline	91	91			
Diesel fuel oil	204	167			
Bunker oil		2, 417	1,952		

最後の機能をしておけるのです せいて 重元 生はる 一世最 まといない ま

Several investigators have studied the pathology produced by oil derivatives. (30, 31, 49, 50, 58, 105, 107, 109, 139, 140, 141, 142) Holland. et al. (49) found that salmonids in naphthalene swim wildly and erratically, and death was prolonged as fish twitched their gill covers and pectoral fins. In phenols, the fish became distressed, lost their equilibrium, and died. Ikuta (50) noted the principal cause of death might be paralysis of the nervous system caused by the toxicity of phenol upon nerves. Flerov (31) found that phenol concentrations of 20 mg/liter had an inhibitory effect upon the normal conditioned reflexes of carp. The sequence of death associated with nonvolatile phenol poisoning in salmon larvae was studied by Vernidub. (139) where he found tetanic convulsions of the body muscles was followed by cardiac failure when the phenol concentration was 1 mg/liter. Bluegill sunfish exposed to 11.5 mg/liter or more of chlorophenol exhibit gross discoloration of the flesh and fish exposed to 18 to 28 mg/liter of phenol exhibit deterioration and discoloration of gill membranes. (58) Waluga, (141, 142) noted both histopathological and hematological changes induced by phenol in bream (Abramis brama). The changes included cell necrosis, nervous system malfunction, hyperaemia, and decreased blood pressure, which led to respiratory failure. Inflammation, necrosis of the gills, circulatory disorders, and damage to the liver, kidney, and heart were noted with phenol poisoning. (105, 107, 140)

There appears to be a carcinogenic effect of some of the oil derivatives as shown by some investigators, (30, 45, 104, 148)

Finkelstein (30) noted papillomatous tumors in eels from the Baltic Sea, and he thought the tumors might be attributable to an accumulation of carcinogenic substances of which ship fuel oil was a major constituent. Carcinomas and papillomas were found on the lips of croakers, a bottom-feeding fish, caught in the Pacific Ocean in an area polluted with carcinogenically potent wastes released from a nearby oil refinery. Young (148) observed papillomas on the body and lips of several types of fish, including the white seabass, (Cynoscion nobilis), the Dover soles (Microstomus pacificus), the white croakers (Genyonemus lineatus), the tongue soles (Symphurus atricauda), the basketweave cusk-eels (Otophidium scrippsae), and Pacific sanddabs (Citharichthys sordidus) from two polluted areas. Tumorous lesions were produced experimentally on the killifish (Fundulus parvipinnis) in twelve days, and the fish died shortly thereafter. These tumors, some of which were cancerous, were never observed on fish taken from unpolluted waters.

Several authors have discussed the indirect effect of motor fuels (28, 129, 149) and oil derivatives such as phenol (29, 54, 82, 96, 105, 120) on the taste of fish. Oil and oil products cause a definite tainting of fish flesh at concentrations that are sublethal to these animals. However, tainting of flesh can be just as detrimental as a lethal dose since it renders them inedible. In some instances a particular chemical may be selectively taken up by certain organs, such as the liver and gills, and therefore leaves the flesh relatively untainted. (120)

Detergents and Emulsifiers. Knowledge of the effects of detergents upon aquatic fauna is important, since these chemicals are frequently applied to clean areas polluted by oil and oil products. The biological effect of all detergents is similar, and their toxicity is about the same according to Reiman. A number of investigators have studied the median tolerance limit (TL) for a wide variety of fish, (12, 21, 26, 44, 47, 49, 59, 61, 77, 86, m 92, 95, 147) and most of these authors agree that detergent concentrations of 5 to 10 mg/liter or more will cause death, while noticable pathological symptoms may be observed in 2 to 3 mg/liter and this may eventually lead to the death of the fish.

Detergents may upset the normal physiology of the fish, as in the case of silver salmon and rainbow trout (49) where symptoms of distress and sluggishness are apparent, along with a loss of equilibrium. excessive slime, opaque corneas, and convulsive twitching of jaws, eyes, and fins. Alevins and young fish placed in detergent solutions exhibited rapid erratic movements and increased respiration, eventually losing equilibrium and floating on their sides before death. (78) A concentration of 1.0 mg/liter of tetrapropylene benzene sulfonate (TPS) caused a decrease in growth and marked liver damage. (84) The gills of fish are very sensitive to the various detergents, as noted by numerous invest'gators. (9, 12, 14, 15, 53, 56, 115, 117, 118) Damage consists mainly of the destruction of the mucous cells of the gill epithelium, (56, 117) causing respiratory folds to stick together. (117) High concentrations of detergents will entirely destroy the epithelium of the gill filaments. (118) Even brief exposure at a high concentration will result in irreverisible gill damage $^{(115)}$ in pumpkin seed sunfish (Lepomis gibbosus). Bock $^{(9)}$ felt that although gill damage would occur at high concentrations, damage to fish under normal environmental conditions is impossible. Nehring (91) noted that all layers of the fish possessing mucous cells, such as the skin, gills, and intestine, were adversely affected by detergents. The apparent loss of mucous cells causes an increased susceptibility of the surviving fish to parasites and disease organisms. (91) Since detergents emulsify oil products, the effect of detergents is to intensify oil pollution effects. (108) Hirsch (48) determined that the toxicity of detergents was due to the length of the alkyl group chain and its position in the aromatic nucleus. The toxicity increases with the number of carbon atoms and levels off after 14 atoms. Even at the lowest detergent concentration tested, marked change in feeding behavior was observed after four days while no such change was noted in the control fish. (32) This change in feeding behavior suggested that the specific effect of the detergent was to inhibit the input of sensory information by which the fish distinguish between palarable, edible material and unpalatable, inedible material. The change is probably caused by damaging the olfactory epithelium in the nasal capsules. These suppositions are corroborated

by histological examinations (7) that show the erosic the fish's taste buds in detergent concentrations as low as 0.5 ppm a lack of regeneration when placed in detergent-free water for silveeks.

Only one commercial oil emulsifier (Tricon Oil Spill Eradicator) has been tested to determine its toxicity to fish. (16) Five striped bass (Roccus saxatilis) were placed in each of eight experimental aquaria and one control aquarium, and it was found that at 65 °F the oil emulsifier was lethal to bass at concentrations as low as 10 ppm (Table 6.1-4). These results show clearly that Tricon Oil Spill Eradicator is toxic to striped bass at low concentrations, and it is probable that lethal concentrations would occur at least locally, if the eradicator were used to treat oil spills.

Detergents may act as solvents that facilitate the penetration of chemicals into the tissues and organs of fish. (80) Experiments with oil and phenol showed that the effect on the taste of fish flesh was definitely and considerably increased by the presence of even small quantities of detergents.

A study by Mann and Schmid (83) has pointed out the possible effects of detergents to the natural reproduction of trout. Detergents stop the movement of trout spermatozoa at concentrations of 5 to 10 mg/liter. If eggs are fertilized in a 5 mg/liter concentration, a high loss of sperm occurs, and all developing eggs die. However, Maldura (78) noted that eggs survived in detergent solutions for several days. The toxicity of various detergents and their effect upon fish eggs has been reported. (56) Continuous flow tests were conducted with flathead minnow eggs to determine the relative toxicity of the surface active agents linear alkylate sulfonate (LAS) and alkyl benzene sulfonate (ABS). (104) The toxicity of both detergents increased with an increased exposure, and LAS was found to be more than twice as toxic as ABS. Marchetti (85) found marked differences in the resistance of successive developmental stages of rainbow trout to the action of a nonionic surfactant. Resistance was greatest shortly after hatching, decreased to a low when yolk absorption was complete, and again increased slightly when the fry began feeding. (78, 85)

TABLE 6.1-4. Toxicity of Tricon Oil Spill Eradicator to Striped Bass (Roccus Saxatilis)(16)

Concentration of Tricon	Sur	vival	
Oil Spill Eradicator, %	Elapsed time	Number of bass alive	Remarks
2.0	7 min	0	All fish showed immediate distress.
0.1	6 min	0	All fish showed immediate distress.
0.05	8 min	0	All fish showed immediate distress.
0.005	30 min 1 hr	2 0	All fish showed distress after about one minute.
0.0016	1 hr 2 hr 3 hr 4 hr 5 hr	5 3 2 1 G	Fish started showing irrita- tion after several minutes.
0.001	4 hr 5 hr 6 hr 8 hr 9 hr 10 hr	5 3 2 2 2	Fish showed first signs of distress at 1 1/2 hr
0.0005	48 hr	5	Fish showed no distress.
0,0005	48 hr	5	Fish showed no distress.
Control	48 hr	5	Fish showed no distress.

Swisher, et al. (132) reported that LAS is relatively toxic to fish when tested under static conditions. However, effluents from continuous flow activated sludge units fed 160 mg/liter of LAS were not toxic to bluegill sunfish fingerlings, nor was there any indication of toxic intermediates being formed during biodegradation.

The effects of synthetic detergents to several marine fish has been studied. (26, 27) It was found that salinity was an important factor in the toxicity of the detergents. The least toxicity occurred at high salinities, and the greatest toxicity occurred in low salinities (Table 6.1-5). Eisler (26) also noted a difference in the toxicity among the different species of fish tested (Table 6.1-6). Mann (81) found that an increase in temperature or an oxygen deficiency accelerates the toxic action of detergents. It was also found that fish developed some resistance to detergents by slow acclimation. The synergistic effects of detergents and pesticides to goldfish was discussed by Dugan. (25) According to Cairns and Scheier, there did not appear to be any synergistic effects between detergents and either temperature or heavy metals, (13) even though Mann found a relationship between temperature and detergents.

TABLE 6.1-5. Effect of Salinity on Toxicity of Three Household Soaps to Mummichogs, Fundulus Heteroclitus (27)

(Sample size is six per group)

	Conc	Concentrations of soaps			
Salinity, °/∞	Control, 0 ppm	Soap A, 1500 ppm	Soap B, 750 ppm	Soap C, 1360 ppm Percent, dead	
	Pel	rcent dead at 48	hr	at 24 hr ^(a)	
5	0	100	100	50	
13	0	33	100	U	
21	0	0	67	0	
29	0	0	0	0	
37	0	0	33	0	
45	0	16	0	0	

⁽a) All dead at 48 hr.

TABLE 6.1-6. Acute Toxicity of a Stock Syndet (Containing 30.3 Per Per Cent ABS-To Five Species of Estuarine Fish. Minimum of Five Test Concentrations Used(26)

	Total number			Total Mean weight weight, per jar,	LC50 in ppm (mg/liter) at various time intervals		
Species	fish	mm	g_	g	24 hr	48 hr	96 hr
Mummichogs	60	38.2	0.62	6.20	23.5	23.5	22.5
Mullet	40	45.8	1.00	8.00	12.0	10.1	10.1
Flounders	20	73.7	4.33	8.66	12.0	10.0	8.2
Eels	60	74.6	0.62	6.20	8.2	8.2	7.5
Silversides	25	58.7	1.43	7.15	7.2	7.2	7.0

Shellfish

The devastation and denudation of marine shellfish by oil, oil products, and the subsequent cleanup procedure with detergents and emulsifiers is an aspect of pollution that has not received study commensurate with the value of the resource, both economic and aesthetic. An improved understanding of oil and chemical tolerance of the marine ecosystem appears needed to provide a rational basis for establishing criteria for oil pollution. Although some understanding of effects exists for molluscan shellfish, less knowledge is available on the effects on crustacean shellfish such as lobsters, shrimp, and crabs. In specific instances, oil pollution and the subsequent use of detergents may not result in excessive shellfish mortality, but economic damage may result from tainting or impaired physiology.

Crude Petroleum. Extensive work has been performed on the effects of crude oil on oysters by the Texas A&M Research Foundation, and much of this has been summarized in a publication by the University of Texas Institute of Marine Science. (73,74) Gowanloch (39) was one of the first people concerned with the effect of oil pollution on shellfish and conducted experiments in which no relationship was found bethen the degree of damage to an oyster bed (said to be polluted) and the distance of that oyster bed from an oil development. However, he felt that oil was a serious problem to shellfish, and his experiments showed a higher incidence of oyster mortality in areas polluted with oil than in nonpolluted areas (Table 6.1-7).

TABLE 6.1-7. Mortality of Oysters Due To Oil Pollution (39)

	<u>Mortalities</u>		
	In Oil Polluted Area	In Nonpolluted Area	
Field experiments	46%	9%	
Laboratory experiments	90%	1 7%	
Laboratory experiments	71%	2%	

Collier (17) exposed oysters to a continuous flow of oil, enough to keep a thick layer of oil on the surface of the water above the oysters. The oil appeared to have no effect on the microorganisms that the oysters probably utilized as food within the experimental rafts. When petroleum was poured onto the water surface, most of the toxic components of the oil evaporated into the air. The minute remainders of toxic compounds did not reach oysters in sufficient concentrations to cause damage or death. The oysters were coated with a greasy material that gave physical evidence that they were in contact with the oil. There was no statistical difference between the growth and mortality of "clean" and "oily" oysters, although the growth was lower and the mortality was higher among those oysters subjected to crude oil. After extensive experiments, Galtsoff, et al. (33) was unable to conclude that oil was a direct cause of oyster mortality, but he felt there was ample evidence to show that the presence of crude oil in water produces conditions inimical to oysters.

The fact that shellfish mortalities and oil pollution occur together does not necessarily mean that the first is caused by the latter. It must be kept in mind that the work of Gowanloch (39) and Galtsoff, et al. (33) was conducted prior to discovery by Mackin, et al. (75) of the fungus. Dermocystidium marinum, that is responsible for extensive oyster mortalities along the Gulf Coast. However, for some reason the subsequent work of Mackin and his coworkers (67, 68, 69, 73, 74, 89) avoids any discussion of this previous work (33, 39) concerning the effect of oil pollution on oysters. Mackin and Sparks (74) studied the effect of a crude oil from an uncontrolled well discharge on oysters. Measurements and records were kept for two years by Mackin and Sparks and they found that the disease incidence, oyster set, growth rate, and general condition were apparently not affected by the oil spillage. In fact, mortality was lower among the "oily" oysters than "clean" oysters (Table 6.1-8). This may indicate that the oil had a useful side effect by eliminating some of the oyster's competitions, predators, or the disease organism itself. The effect produced by releasing 10,000 tons of crude oil on the shore of Guanica. Puerto Rico was described by Diaz-Piferrer. (20) The damage by the oil was extensive and marine organisms suffered tremendous mortalities, among which were adult and juvenile lobsters, crabs, sea urchins, starfish, sea cucumbers, snails, ocotopuses, and squids.

TABLE 6.1-8. Oyster Mortality Due To Crude Oil From A Wild Well (74)

Station	Total mortality (using 1000 oysters)			Total mortality (300 oysters)	
Area	No.	Percent	Mean	Percent	Mean
Oil Area	1 2 3 4	65.1 59.0 61.2 30.4	53.9	60.7 52.7 65.0 28.3	51.7
Control Area	5 6 7	48.0 80.7 63.5	64.1	42.3 79.7 55.0	59.0

Mackin and Sparks (74) noticed that it took two months for oysters to lose the oily taste that they had acquired from the crude oil. This could cause definite economic loss of a shellfish resource that is harvested on an annual basis. Such was the case in Yaquina Bay, Oregon, when between 185,000 and 425,000 gal. of oil were lost in 1963. Crabs caught throughout the bay were contaminated and had an oily taste. (126) Because of this, all bay crab fishing, both sport and commercial, stopped, resulting in an economic loss to the commercial crab fishermen. In the laboratory it was found that it takes crabs (Cancer magister) one week in pure salt water to clean all of the oil off their bodies. However, this did not occur in the bay, since it was covered with oil on most of the 11 miles of its bottom. The local oyster company also closed down because of the oily flavor in the oysters (Ostrea lurida and Crassostrea gigas) that made them unmarketable. Cil was also found over the clam beds in Yaquina Bay, but the extent of damage and tainting to these animals was not ascertained. An oily taste in oysters (C. virginica) may be acquired by as little as 0.01 ppm oil. (88) It may be retained for four to six months, and the time required for clearing the oily taste is influenced by the size of the original dosage of oil and the persistance of oil in the vicinity of the shellfish. (88) Hawkes (42) noted that quahogs (Venus mercenaria) are not killed or harmed by oil pollution, but that they have a taste and odor that is repugnant. Tainting of European mussel beds by oil has caused serious problems, (42) and tainting of clams, oysters, and cockles may be a problem. (124)

Many cyster mortalities in the Gulf area, thought to be due to crude oil, were found to be due to elevated salinities and temperatures. (73) Examination of oil contaminated shores by George (35) showed that barnacles (Elminius modestus, Balanus balanoides, and Chthamalus stellatus) and limpets (Patella vulgata) appeared to be unharmed although they were covered with oil. It was inferred that the limpets may assist in eliminating the oil by their intake of oil and subsequent breakdown of it as they browsed. There was no decrease in the limpet population in the contaminated area and it was, therefore, assumed that the oil was nontoxic to these molluscs. Observations of the beaches contaminated by oil from the TORREY CANYON corroborated these findings. (37, 93, 100) Glude (36) noted that actual loss of commercially important shellfish due to oil from the TORREY CANYON was negligible, largely because of fortuitous circumstances which prevented the contamination of shellfish estuaries. However, he felt that similar oil spills under the proper conditions could have disasterous effects upon commercial shellfish resources. Some oil did reach one oyster growing area, but since it was limited and the oysters were not to be harvested for several months, the effect, including tainting, is thought to be very small. Oil was found to be toxic to a variety of plankton, including the crustacean Gammarus, and in combination with low oxygen there is an adverse synergistic effect. (87) Nelson-Smith (93) found that cockles (Cardium edule) failed to survive fresh crude oil at a concentration of 0.05% and gastropods (Littorina littorea) were particularly sensitive to crude oil, but sand-shrimps (Crangon vulgaris) and prawns (Leander serratus) were able to tolerate 0.1% of crude oil. From this it is apparent that fresh crude oil which contains some of its toxic volatile aromatic constituents has a definite deleterious effect upon both molluscan and crustacean shellfish.

ĭ

I

According to Galtsof⁽³⁴⁾ the pumping rate is reduced or stopped when oysters are placed in either crude oil or the soluble components of oil. It interferes with the ciliary beat, which in turn reduces the ability of the animal to pump and feed. Lunz⁽⁶⁶⁾ found that the pumping rate of oysters was effected by 1% "bleedwater" from oil explorations in Louisiana and was greatly impaired by 5 to 10% "bleedwater". Lund⁽⁶⁵⁾ corroborated the work of Lunz.⁽⁶⁶⁾ but found that crude oil had no

noticable effect upon the oyster's pumping rate. Hence, he disagreed with the work of Galtsoff. (34) This may be explained by the fact that there was a difference in the toxic portion of crude oil used by these two investigators. The work of Alyakrinskaya (151) on sea mussels (Mytilus galloprovincialls) supports this supposition. He found these molluscs can withstand crude oil in concentrations up to 20 ml/liter, but that concentrations of oil exceeding that level have a deleterious effect on the physiological behavior of these animals. He felt the reason this mollusc could tolerate high concentrations of crude oil was because the ciliated epithelium of the gills and mantle were highly resistant to the inimical effects of the oil. Minute amounts of toxic chemicals that are not lethal to shellfish may seriously interfere with the normal physiology of these animals. (10, 11) Chipman and Galtsoff (19) found a species difference in susceptibility to crude oil, diesel oil, and fuel oil. All three were found to be toxic to barnacles (Balanus balanoides) and oysters (Crassostrea virginica), while there was no apparent effect upon the hard shell clam (Venus mercenaria). It was thought that this lack of toxicity to V. mercenaria was due to an insufficient amount of the oils used. (19) However, these experiments indicate that there may be a very definite difference in susceptibility among the various species of shellfish.

Oil Products and Derivatives. Oglesby and Sylvester (99) made a detailed study to determine the effects of an oil refinery effluent on the intertidal marine life. They observed that there was no noticeable effect of the refinery's effluent upon any of the intertidal invertebrates, including both commercial and noncommercial species. Menzel and Hopkins (90) showed that there is an adverse effect of "bloedwater" upon oysters, but that the effect is confined to within 150 ft of the effluent. There was a higher mortality and slower growth rate among oysters within this area than among those at distances greater than 150 ft. Mackin (70, 72) found that the effect of oil drilling mud was toxic to oysters over an extended period of time in heavy concentrations. However, the concentrations usually encountered in the environment have only a mildy toxic effect, and barnacles and young oysters were able to grow free of apparent mortality, decrease in feeding activity, or increased susceptibility to disease. The toxic effect that turpentine has on oysters (C. gigas) is to make them more

susceptible to disease and invasion by otherwise nonpathogenic organisms. (101) It is thought that gasoline and other petroleum products may have a similar affect on shellfish. Motor exhaust gases were found to be highly toxic to oysters. The degree of mortality was 6.5 times greater among experimental groups than in the control groups. (71) The toxicity of several oily wastes on <u>Daphnia magna</u> has been reported by Anderson, (1) and he noted that phenol was highly toxic in quantities of 94 ppm.

Shaw and Timmons (122) note that the concentration (300 ppm) of emulsified aromatic hydrocarbons used to destroy weeds in irrigation ditches was sufficient to eliminate crayfish from the ditches. Tendron (135) noted that shellfish, although alive, may be unfit for consumption because of pollution by the carcinogenic hydrocarbon 3, 4-benzpyrene found in their bodies. Oysters that were heavily polluted and contaminated with ship fuel oil contained 3, 4-benzpyrene, a carcinogen. (18) Barnacles attached to creosoted poles located in marine waters contained the same carcinogenic hydrocarbon (3, 4-benzpyrene), and it elicited sarcomas in mice when extracts from the barnacles were injected into the mice. (121) Hueper (45) noted the endemic occurrence of pappillary tumors around the rectal opening of soft shell clams (Mya arenaria), but he did not feel these were due to oil pollution, even though the clams were taken from waters adjacent to areas highly polluted by ship fuel oil. Schafer (113, 114) has reported changes in the amino acid content of the bay mussel (Mytilus edulis), the abalone (Haliotis cracherodii), and the crab (Pachygrapsus crassipes) due to organic pollution, Most notable was the complete lack of asparagine in the animals taken from polluted waters. It is felt that the alteration of the amino acids is probably in some way responsible for the reputed flavor change occurring in H. cracherodii taken from polluted waters. Young (148) noted that H. cracherodii taken from polluted waters weighed significantly less than those taken from unpolluted areas, but there was no apparent difference in mortality.

The effects of 2, 300, 000 gal of assorted grades and brands of gasoline diesel fuel, and furnace oil on the marine environment has been described by Lindsay and Tegelberg. (60, 134) In 1963, an oil and gas barge was stranded at Moclips, Washington. Because of the important razor clam (Siliqua patula) beaches that support both a commercial fishery and a large

sport fishery in the vicinity, a detailed study was made. Contamination and mortalities caused the closure of the commercial season after just 2 days and after a catch of only 11,000 lb of clams, 9% of the commercial quota, Because the Washington State Department of Fisheries makes regular population estimates of the razor clam areas, they were able to make an accurate evaluation of the extensive mortalities. At low tide, oil was seen in the surf and on the beach when oil was pumped overboard to lighten the barge in an attempt to salvage it. This deliberate pumping was done under protest by the Washington State Department of Fisheries, and a daily record of dead clams was kept for litigation purposes. In addition to dead razor clams, lesser amounts of horse clams (Schizothaerus nuttalli) and Dungeness crabs (Cancer magister) were found dead on the beaches (Table 6.1-9). Special precautions were taken to avoid duplication of mortality counts. Measureable amounts of ethylene dichloride, a gasoline additive, were found in the clam meats. Two major mortality peaks were apparent. The first occurred two days after the initial spill when the barge ran aground, and the second occurred three days later after the deliberate pumping of oil overboard. The mortalities among razor clams were extended over 20 miles of beach, and therefore, the estimated mortality figure of 300,000 clams is considered conservatively low due to the difficulty of covering the entire beach area and trying to avoid duplication. Dead clams were noted washed up on the beach. dead or inactively drifting in the surf, and normally positioned in the sand but with their necks extended in an uncontrolled manner. There was undoubtedly some loss of young razor clams (2 to 30 mm) that were small enough to escape detection. Most of the spawning occurred after the gas and oil dissipated and there was no deleterious affect to the 1964 set of young clams. A loss of over 50% of the available razor clams was evident one-half mile from the oil barge, and a 37% mortality was evident three and one-half miles from the barge. Under less favorable circumstances an accident such as this could completely decimate the population of a razor clam beach.

A similar accident was reported by North, et al. (97,98) when a cargo of about 60,000 barrels of diesel oil began leaking from a grounded ship into an estuarine cove. The luxurious submarine gardens in this cove and the surrounding beaches perished, and the shore was littered with dead and dying animals. The TAMPICO wreck created a situation wherein a

completely natural area was almost totally destroyed suddenly. On nearby beaches, dead Pismo clams (Tivela stultorum) littered the shore for a month after the wreck. In addition to the dead animals washed ashore, many more were adrift subtidally and decomposed on the sea floor. Only a few animal species survived, the two most prominent being a tiny smail (Littorina planaxis) (removed from the pollution effects by its location above the high water mark) and a large green anemone (Anthopleura xanthogrammica). Among the dead species were lobsters, abalone, sea urchins, starfish, mussels, clams, and other smaller animals. The area is an isolated marine environment where man's activities are negligible. Gradually, over a period of ten years, the various marine animals have again established themselves in the cove. Sixty-nine species of animals have been observed, compared to only two species immediately after the shipwreck. In spite of the reestablishment of lost species, the cove is not the same as it was prior to the disaster. (98) Many species have recently appeared, and often only one or two specimens have been seen while prior to the wreck these same species were abundant. This study indicates the time scale for recovery.

TABLE 6.1-9. Summary of Investigations of a Razor Clam Kill Resulting from Petroleum Spillage at Moclips: March, 1964.

Date	Dead Razor Clams	Miscellaneous Dead Invertebrates	Dead Horse Clams	Dead Crabs
13 March 1964	4, 000	NR	NR	100
14 March 1964	140, 437	NR	NR	2
15 March 1964	1, 500	NR	NR	NR
16 March 1964	1, 500	Yes	Yes	56
17 March 1964	121,000	Yes	Yes	Yes
18 March 1964	10, 000	NR	NR	Yes
19 March 1964	6, 640	NR	NR	NR
20 March 1964	8, 100	NR	NR	NR
21 March 1964	4, 880	NR	NR	NR
22 March 1964	<u>Few</u>	NR	NR	NR
Total	298, 057			

⁽a) NR--None Reported

Detergents and Emulsifiers. Emulsifiers are commonly used to remove oil and grease from shorelines and from water surfaces. It is usually claimed by the manufacturers of these products that they are nontoxic, but laboratory studies tend to refute these claims. Dowden (24) found that crude oil was less toxic to Daphnia than either of two emulsifiers or the emulsions formed by them with crude oil. The toxicity of crude oil to Daphnia was attributed to the entrapment of these animals at the surface of water. The emulsion was more toxic than the emulsifier alone. Emulsifiers were found to be more toxic than foaming agents to Daphnia. In laboratory studies of the effects of alkyl benzene sulfonate (ABS) on aquatic invertebrates (130), it was found that crayfish (Orconectes rusticus), freshwater shrimp (Synurella sp.), and Son bugs (Lirceus sp.) were seriously reduced in numbers by exposure to 10 ppm ABS over a period of two weeks or more. A snail (Goniobasis sp.) was apparently unaffected by this concentration (Table 6.1-10). Cairns, et al. (15) found that there was 100% survival among snails (Physa) subjected to 24 mg/liter of ABS. Nehring (92) gives the toxicity threshold of various flotation agents to the crustaceans Daphnia and Gammarus.

Concentrations of surfactants too low in themselves to cause direct harm to aquatic animals may combine with low levels of other pollutants and be very detrimental. Because the larvae of molluscs are more sensitive to environmental changes than the adults, Hidu (46) studied the effects of various synthe is surfactants on the larvae of clams (Venus mercenaria) and oysters (C. virginica). The development of fertilized eggs and growth and survival of fully formed veliger larvae of clams and oysters was reduced by concentrations of surfactants between 0.01 and 5.00 mg/liter (see Table 6.1-11). The cationic surfactants were the most toxic, the anionic surfactants were intermediate in toxicity, and the nonionic surfactants were the least toxic. Clam larvae were less sensitive to surfactants than were oyster larvae. Reduction in the rate of growth of larvae of clams and oysters occurred at lower concentrations than those required to produce death. Fertilized eggs were always killed at lower concentrations of surfactants than those producing mortality in fully grown veliger larvae. Calabrese and Davis (152) found that the percentage of fertili. I oyster eggs developing normally was reduced significantly at concentrations greater than 0.025 and 0.25 mg/liter

TABLE 6.1-10. Effects Alkyl Benzene Sulfanate on a S cam Mollusc

		Goniobasis sp.	
Tank Number	ABS Concent ation, ppm	Initial Number , August 2-14	Percent Survival, August 2-14
1	0	20	95.0
2	0	20	100.0
3	4	20	100.0
4	4	20	85.0
5	8	20	100.0
6	8	20	90.0
7	16	20	40.0
8	16	20	80.0
9	32	20	0
10	32	20	ŋ

of active LAS and a commercial liquid biodegradable detergent, respectively. The percentage survival of larvae decreased significantly at 1.00 mg/liter for LAS and at 2.50 mg/liter of the liquid detergent. Growth of oyster larvae was significantly reduced at 0.50 mg/liter for LAS and at 2.50 mg/liter of the liquid detergent. Based on his experimental work, Hidu (46) felt that concentrations of surfactants that would be detrimental to clam and oyster larvae may be reached in certain commercial shellfish areas, because the surfactants may accumulate in the estuarine waters not subjected to extensive tidal flushing.

George (35) stated that in some cases commercial emulsifiers would be an acceptable cleanup procedure, but suggested it is both wasteful and unpocessary to use emulsifiers on shores that may have marine life of commercial value, because oil films are fairly quickly removed or rendered nontoxic by natural processes. However, emulsifiers are capable of destroying all of the limpets (Patella vulgata) and 80 to 95% of the acorn barnacles, and they are extremely toxic to all other forms of intertidal life. Glude noted that adverse biological effects from the TORREY CANYON were increased by the application of detergents that were highly toxic and should be avoided if possible. (36) In a later more detailed report, Glude and

TABLE 6.1-11. Mean Concentrations Affecting Larvae Growth and Survival in Juvenile Shellfish

	Concentration, mg/liter active ingredient				
	Clams		Oyster		
Type	Mean ^(a)	Range	Mean	Range	
Anionic Alkyl aryl sulfonate	1.55	0.55-3.00	0.76	0.14-1.50	
Alkyl sulfate	1.22	0.73-1.46	1.07	0.29-1.46	
Cationic	0.34	0.01-1.00	0.25	0.05-0.50	
Nonionic	2.66	1.00-5.00	2.00	1.00-2.50	
For all surfactants	1.44	0.01-5.00	1.02	0.05-2.50	

⁽a) Means were compiled by averaging lowest concentrations of all compounds compounds tested that significantly reduced, in all replicate experiments, survival of developing embryos and growth and survival of developed veliger larvae.

Peters (37) reported that it was indeed very fortunate that the areas contaminated by oil were places containing no commercial shellfish resources. However, the pernicious effects of the detergents could be seen in the tide pools that contained marine fauna in England. The thousands of gallons of detergent used to emulsify the oil reduced mussel populations to one-third or one-tenth of their original number, and in many places only the byssal threads of these animals remained to indicate the extent of damage to the former mussel population. Very few mussels were probably able to remain closed until the tide returned to dilute the detergents. Very few live limpets were observed in the detergent treated areas, and it was apparent that they had been decimated by the effects of the detergent. In France, the application of detergents was avoided because of its adverse effect on marine resources. French authorities condemned the British for applying great quantities of detergent at sea. They maintained that this greatly increased the severity of the problem when the floating mixture reached the French coast. The French used detergents on areas that were important to tourism but not to fisheries.

Following the TORREY CANYON disaster, O'Sullivan and Richardson (100) made a report of the subsequent effect upon the marine fauna by the application of detergents. They made a comparison survey of

two areas contaminated with oil: one that was left untreated and one that was treated with detergents. The untreated areas showed no fish or invertebrate mortalities, while the treated area had an almost complete lack of snails, limpets (Patella vulgata), and barnacles: those remaining alive were in a weakened condition. The detergents used had a deleterious effect upon shrimp and crabs. (75) The sea anemones appear to be resistant to oil and partially resistant to detergent pollution. (37. 98. 100) Since the detergents are highly toxic and make the oil harmful by bringing it into an emulsion, the use of detergents to clean up oil in areas with marine life constitutes a cure worse than the disease itself. (100) However, Simpson (124) feels that even though the detergents and emulsifiers are highly toxic to marine life, their use would not be deleterious to the fauna, provided they were not used in estuaries where dilution and dispersal would be at a minimum. Along with the oil, the detergents may give a tainted flavor to shellfish. (37,124)

Nelson-Smith (93,94) describes several oil spills and their subsequent clean up effects on the marine fauna. While snails (Littorina littorea) may be eliminated by detergent application, scallops (Pecten maximus) living on the shallow bottom were unharmed. Following the Milford Haven detergent incident, there was a heavy mortality among snails, crabs, shrimp, and mussels. A few animals, such as snails and bivalves which may close tightly, are able to protect themselves for short periods of time against the effects of the detergents, but protracted exposure to high concentrations of detergents are lethal even to these animals. Animals unable to shut out the detergents are immediately affected and subsequently die. The detergents and emulsifiers, although toxic themselves, allow the oil and its toxic portions to penetrate the protective mucous and water coating of most marine animals that would in many cases render the oil inert. (93) Many populations appear most vulnerable at their upper and lower most tidal range extensions, where the environmental limitations have combined with detergents to produce a synergistic effect. (93)

Literature Cited Concerning Oil Pollution and Fish and Shellfish

- 1. Anderson, B. G. "The Toxicity Thresholds of Various Substances Found in Industrial Wastes as Determined by the Use of Daphnia Magna," Sewage Works Journ., vol. 13, p. 1156, 1944.
- 2. Anonymous. Report on Oily Substances and Their Effects on the Beneficial Uses of Water, Calif. State Water Poll. Control Bd., Publication No. 16, p. 71, 1956.
- 3. Anonymous. The Pollution of Water by Detergents, Organization for Economic Cooperation and Development, Paris, 86 pp. 1964.
- 4. Anonymous. Bibliography on Synthetic Detergents in Water and Wastes Including Analytical Methods and Physiological Effects, Pub. Health Service, R. A. Taft San. Eng. Center, Cincinnati, Ohio, 91 pp. 1964.
- 5. Anonymous. Pollution-Caused Fish Kills in 1964, U. S. Depart. of Health, Education, and Welfare, Public Health Service Publ. No. 847 (revised), 28 pp. 1964.
- Anonymous. "The Battle for Britain's Beaches," <u>Life Magazine</u>, pp. 8-28. April 17, 1967.
- 7. Bardach, J. E., M. Fujiya and A. Holl. "Detergents: Effects on the Chemical Senses of the Fish <u>Ictalurus natalis</u>," <u>Science</u>, vol. 148, p. 1605. 1965.
- 8. Beadles, J. K. The Effect of Domestic and Oil Refinery Effluents on Meristic and Morphometric Characteristics of Three Cyprinind Fishes, Subm. to faculty of Graduate School Oklahoma State Univ. in partial fulfillment of requirements for degree of Doctor of Philosophy, p. 86. May, 1966.
- 9. Bock, K. J. "Uber die Wirkung von Washchronhstoffen auf Fische," Arch. FischWiss, Germany, 17(1), pp. 68-76. 1986.

٠.

- 10. Butler, P. A. "Reaction of Estuarine Mollusks to Some Environmental Factors," Biological Problems in Water Pollution, Third Seminar, U. S. Public Health Service, Cincinnati, Ohio, pp. 92-104. 1932.
- 11. Butler, P. A., A. J. Wilson, and A. J. Rick. "Effect of Pesticides on Oysters," Proc. Natl. Shellfish. Assoc., vol. 51, pp. 23-32, 1960.
- 12. Cairns, J. and A. Scheier. "The Acute and Chronic Effects of Standard Sodium Alkyl Benzene Sulfonate Upon the Pumpkinseed Sunfish. Lepomis gibbosus (Linn.) and the Bluegill Sunfish, L. Macronchirus," R. of Proc. 17th Indust. Waste Conf., Eng. Bull. Purdue Univ. Eng. Ext. Series, vol. 112, p. 14, 1963.

- Cairns, Jr., J. and A. Scheier. "The Effects of Sublethal Levels of Zinc and of High Temperature Upon the Toxicity of a Detergent to the Sunfish, Lepomis gibbosus (Linn.)," Notulae Naturae, vol. 367, pp. 1-4. 1964.
- 14. Cairns, Jr. J. and A. Scheier. "The Effect of Exposure to ABS Detergent Upon the Blood Chloride Regulation of the Pumpkinseed," Progr. Fish-Cult., 28(3), pp. 128-132. 1966.
- 15. Cairns, Jr. J., A. Scheier and N. E. Hess. "The Effects of Alkyl Benzene Sulfonate on Aquatic Organisms," Ind. Water & Wastes, vol. 9, pp. 22-8. 1964. Publ. Health Eng. Abs., vol. 44, p. 1587.
- 16. Chadwick, H. K. "Toxicity of Tricon Oil Spill Eradicator to Striped Bass," Calif. Fish Game, vol. 46, pp. 373-374. 1960.
- 17. Collier, A. Oysters, Their Growth Rate and Survival When Retained Under Crude Petroleum. Unpubl. Rept., Gulf Refining Company, p. 158, 1953.
- 18. Cahnman, H. S. and M. Kuratsune. "Determination of Polycyclic Aromatic Hydrocarbons in Oysters Collected in Polluted Water," Anal. Chem., vol. 29, pp. 1312-1317, 1957.
- 19. Chipman, W. and P. S. Galtsoff. "Effects of Mixed Oil With Carbonized Sand on Aquatic Animals," U. S. Fish Wildlife Serv. Spec. Sci. Rept. 1, p. 50. 1949.
- 20. Diaz-Piferrer, M. "The Effects of an Oil on the Shore of Guanica, Puerto Rico," The 4th Meeting Assn, Island Mar. Labs... Curacao, vol. 4, pp. 12-13. November, 1962.
- 21. Dooley, T. P. and J. Cavil. "Minimum Lethal Concentration of 15 Common Detergents on the Mosquito Minnow (Gambusia affinis)," Texas Jour. Sci., 16(2), pp. 202-209.
- 22. Douglas, Neil H. "A Study of the Comparative Use of Different Species of Fish in the Bioassay of Petroleum Refinery Effluents," Proc. 14th Ann. Conf. S. E. Assoc. Game and Fish Comms., pp. 215-222, 1961.
- Douglas, N. H. and W. H. Irwin. "Evaluation and Relative Resistance of Sixteen Species of Fish as Test Animals in Toxicity Bicassays of Petroleum Refinery Effluents," Proc. 17th Industr. Waste Conf. Purdue Univ. Engng. Extn. Ser. No. 112, pp. 57-76, 1962. Water Poll. Abs., 37(4), Abst. No. 668, 1964.
- 24. Dowden, B. F. "Toxicity of Commercial Waste-Oil Emulsifiers to Daphnia magna," J. Wat. Pollut, Contr. Fed., vol. 34, pp. 1010-1014, 1962. Water Poll. Abs., 36(3), abst. No. 520, 1963.

- Dugan, Patrick R. "Influence of Chronic Exposure to Anionic Detergents on Toxicity of Pesticides to Goldfish," <u>Journal WPCF</u>, vol. 39, no. 1, pp. 63-71, 1967.
- Eisler, R. "Some Effects of a Synthetic Detergent on Estuarine Fish," Trans. Amer. Fish. Soc., vol. 94, pp. 26-31, 1965.
- 27. Eisler, R. and D. G. Deuel. "Acute Toxicity of Soaps to Estuarine Fishes," Progve Fish Cult., vol. 27, pp. 45-48, 1965.
- 28. English, J. N., G. N. McDermott, and C. Henderson. "Pollutional Effects of Outboard Motor Exhaust--Laboratory Studies," J. Wat. Pollut. Contr. Fed., vol. 35, pp. 923-931. 1963.
- 29. English, J. N., E. W. Surber, and G. N. McDermott. "Pollutional Effects of Outboard Motor Exhaust--Field Studies," J. Wat. Poll. Contr. Fed., vol. 35, pp. 1121-1132. 1963.
- 30. Finkelstein, E. A. Tumors of Fish. Arkh. Patol, vol. 22, pp. 56-61, 1960.
- 31. Flerov, B. A. "Effect of Phenol on the Conditioned Reflex Activity of Fish," Gidrobiol. Zh., Akad. Nauk Ukr SSR, 1(3), pp. 49-50. 1965. Chem. Abst., vol. 63, p. 10370b.
- 32. Foster, N. R., A. Scheier, and J. Cairns, Jr. "Effects of ABS on Feeding Behavior of Flagfish, Jordanella floridae," Trans. Amer. Fish. Soc., 95(1), pp. 109-110.
- 33. Galtsoff, P. S., H. F. Prytherch, R. O. Smith, and V. Koehring. "Effects of Crude Oil Pollution on Oysters in Louisiana Waters," Bull. U. S. Bur. Fish, 48(18), pp. 142-210. 1935.
- 34. Galtsoff, P. S. "Environmental Factors Affecting Oyster Populations,"

 The American Oysters, Crassostrea virginica Gmelin, U. S. Fish & Wildlife Service, Fish. Bull., vol. 64, pp. 397-456, 1964.
- 35. George, M. "Oil Pollution of Marine Organisms," Nature, vol. 192, pp. 1209. 1961.
- 36. Glude, J. B. "The Effects of Oil From the Wrecked Tanker TORREY CANYON on Shellfisheries Resources of England and France," Proc. Natl. Shellfish Assoc., vol. 58; (abstract only). 1967.
- 37. Glude, J. B. and J. A. Peters. Observation on the Effect of Oil from the Tanker TORREY CANYON and Oil-control Measures on Marine Resources of Cornwall, England and Brittany, France. Unpublished Rept. Submitted to the Director of the Bureau of Commercial Fisheries. 33 pp. 1967.

- 38. Gould, Wm. R., Troy C. Dorris. "Toxicity Changes of Stored Oil Refinery Effluent," J. Water Poll. Cont. Fed., pp. 1107-1111, 1961.
- 39. Gowanloch, J. N. "Pollution by Oil in Relation to Oysters," Trans. Amer. Fish. Soc., vol. 65, pp. 293-296. 1935.
- 40. Graham, R. J. Long-term Toxicity Bioassay of Oil Refinery Effluents, Doctor of Philosophy Thesis, Okla. State Univ.,
- 41. Gregg, R. "Analysis of Fish Kills Natural and Man-made," Sew. Water Works Jour., vol. 46, no. 10, 16, and 18. 1965. Water Poll. Abs. (Brit.), vol. 39, p. 1409. 1966.
- 42. Hawkes, A. L. "A Review of the Nature and Extent of Damage Caused by Oil Pollution at Sea," Trans. N. Amer. Wildlife Conf., vol. 26, pp. 343-355, 1961.
- 43. Heinz, H. J. and W. K. Fischer. "Detergents in Water and Sewage," Fette Seif. Anstrichm, vol. 64, p. 270. 1963. Public Health Eng. Abstr., vol. 43, p. 1531. 1963.
- 44. Henderson, C., Q. H. Pickering, and J. M. Cohen. "The Toxicity of Synthetic Detergents and Soaps to Fish," Sewage and Industrial Wastes, 31(3), pp. 295-306. 1959.
- 45. Hueper, W. C. "Environmental Carcinogenesis in Man and Animals," Ann. N. Y. Acad. Sci., vol. 108, pp. 963-1038. 1963.
- 46. Hidu, H. "Effects of Synthetic Surfactants on the Larvae of Clams (M. mercenaria) and oysters (C. virginica)," Jour. Water Poll. Cont. Fed., vol. 37, pp. 262-270. 1965.
- 47. Hirsch, E. "Structure Elements of Alkylbenzenesulphonates and Their Effect on the Behaviour of Fish," Vom Wass., vol. 30, pp. 249-259. 1963.
- 48. Hirsch, E. "The Biological Behaviour of Surfactants. II. The Correlation Between Chemical Constitution of Alkylbenzenesulfonates and Their Effects on Fish," Fette, Seifen, Anstrichmittel, vol. 45, p. 914, 1963. Chem. Abs., vol. 60, p. 5935, 1964.
- 49. Holland, G. A., J. E. Lasater, E. D. Neumann, and W. E. Eldridge. Wash. State Dept. Fish., Res. Bull., No. 5, 264 pp. 1960.
- 50. Ikuta, K. "Studies on the Massive Death of Ayu, Plecoglossus altivelis T. and S., Caused by the Waste of Phenol-Formaldehyde Resin Works," Bull. Japanese Soc. Sci. Fish., 30(8), pp. 601-609, 1964.

Ĭ

- 51. Irwin, William H. "Fifty-seven Species of Fish in Oil-Refinery Waste Bioassay," <u>Transactions of the Thirtieth North American Wildlife and Natural Resources Conference, Wildlife Management Institute.</u> Wash. D. C., pp. 89-99, 1965.
- 52. Jenkins, Charles Robert. A Study of Some Toxic Components in Oil Refinery Effluents, Oklahoma State Univ., Doctor of Philosophy Thesis. 72 pp. 1964.
- 53. Kiess, F. "Problems in Water Pollution Control," Gas-Wasserfach. 104(50), p. 1443. 1963. Chem. Abs., vol. 60, p. 9003. 1964.
- 54. Klinke, H. R. "Effects of Oil and Tar Products in Water on the Fish Organism," Münch. Beitr., vol. 9, pp. 75-81, 1962. Water Poll. Abs., 37(6), Abst. No. 1018, 1964.
- 55. Klinke, H. R. "Phenol Content in Water and its Effect on the Fish Organism," Arch. FischWiss. (Germany), vol. 16, pp. 1-16. 1965, Water Poll. Abs. (Brit.). vol. 39, p. 1009, 1966.
- 56. Klust, G. and H. Mann. "Detergents and Fisheries," Allg. FischZtg, vol. 87, no. 3, 1962. LitBer. Wass, Abwass, Luft u. Boden, vol. 11, p. 122. 1962/3, Water Poll Abs., (Brit.), vol. 37, p. 1009. 1964.
- 57. Krombach, H. and J. Barthel. "Investigation of a Small Watercourse Accidentally Polluted by Phenol Compounds," Intern. J. Air Water Pollution, vol. 7, p. 39. 1963. Public Health Eng. Abs., vol. 43, p. 1343.
- 58. Lammering, M. W. and N. C. Burbank. "The Toxicity of Phenol, 0-Nitrophenol to Bluegill Sunfish." Proc. 15th Industr. Waste Conf., Purdue Univ. Engng Extn. Ser. No. 106, pp. 541-555, 1980. Water Poll. Abs., 35(1), Abst. No. 179, 1982.
- 59. Lemke, A. E. and D. I. Mount. "Some Effects of Alkyl Benzene Sulfonate on the Bluegill, Lepomis macrochirus," Trans. Amer. Fish. Soc., 92(4), pp. 372-378. 1963.
- 60. Lindsay, C. E. and H. C. Tegelberg. <u>Razor Clam Mortalities at Pacific and Copalis Beaches</u>. March 1934, Unpubl. Rept., Wash. State Dept. Fisheries, p. 22. 1964.
- 61. Ludemann, P. and H. Kayser, "Contribution on the Toxicity of Surface-Active Substances (detergents) to Fish," Z. Angew, Zool., vol. 50, pp. 229-238, 1963.
- 62. Luk'yaneko, V. I. and B. A. Flerov. "Reversibility Dynamics of Phenol Poisoning in Carp," Mater. Biol. Bidrol. Volzh. Vodokhr., Akad. Nauk SSSR, pp. 107-110. 1963. Water Poll. Abs. (Brit.), 38(8), p. 1377. 1965.

- 63. Luk'yanenko, V. I. and B. A. Flerov. "Test Data on Toxicology of Aging Fish," Farmakol. i Toksikol., 26(5), p. 625, 1983. Chem. Abs., vol. 60, p. 13626, 1964.
- 64. Luk'yanenko, V. I. and Flerov, B. A. "The Effect of the Seasonal Factor in the Resistance of Fish," Vop. Ikhitol., vol. 4, pp. 178-183. 1964. Biol. Abstr., vol. 46, p. 5219. 1965.
- 65. Lund, E. J. "Effect of Bleedwater, Soluble Fraction and Crude Oil on the Oyster," <u>Institute of Marine Sci.</u>, IV(2), pp. 328-329. July 1957.
- 66. Lunz, G. R., Jr. "The Effect of Bleedwater and of Water Extracts of Crude Oil on the Pumping Rate of Oysters," 107 pp. (mimeo), 1950.
- Mackin, J. G. The Effect of Crude Petroleum on Oysters Heavily Infected with Polydora, Clinoa, and Martesia, Texas A&M Research Foundation Project Nine Report, 1950.
- 68. Mackin, J. G. A Report on Three Experiments to Study the Effect of Oil Bleedwater on Cysters Under Aquarium Conditions, 5 pp. (mimeo). April 11, 1950.
- 69. Mackin, J. G. A Comparison of the Effect of Application of Crude Petroleum to Marsh Plants and to Oysters, 4.pp. (mimeo). April 12, 1950.
- 70. Mackin, J. F. Studies on the Effect of Quebracho on Oysters, Project 23 Rept. Texas A&M College, Tech. Rept. No. 1, 6 pp. (memo). 1951.
- 71. Mackin, J. G. A Study of the Effect of Motor Exhaust Gases on Oysters, Texas A&M Research Foundation. Tech. Rept. No. 4 Project 23, 4 pp. (memo). 1952.
- 72. Mackin, J. G. Studies on the Effect of Drilling Mud-Graphite Mixtures on Oysters, Tech. Rept. No. 20, Project 23, 3 pp. (mimeo). 1957.
- 73. Mackin, J. G. and S. H. Hopkins. "Studies on Oyster Mortality in Relation to Natural Environments and to Oil Fields in Louisiana," Publ. Inst. Mar. Sci., vol. 7, pp. 1-131. 1962.
- 74. Mackin, J. G. and Sparks, A. K. "A Study of the Effect on Oysters of Crude Oil Loss from a Wild Well," Publ. Institute of Marine Sci., Texas, vol. 7, pp. 231-261. July 1962.
- 75. Mackin, J. G., H. M. Owen, and A. Collier. "Preliminary Note on the Occurrence of a New Protistan Parasite, <u>Dermocystidium marinum</u> n. sp. in <u>Crassostrea virginica</u> (Gmelin), Science, vol. 111, pp. 328-329, 1950.

- 76. Malacea, L. Cure, V., and Weiner, L. "Contributions to the Knowledge of the Noxious Action of Oil., Napthenic Acids and Phenols on Certain Fish and Crustacean Daphnia magna." Straus. Stud. Prot. Epur. Apel (Romania), vol. 5, p. 353. (English summary), 1954. Water Poll. Abs. (Brit.), vol. 38, p. 1565, 1965.
- 77. Maldura, C. "Preliminary Research on the Action of Alkylarylsulphonate on Salmo irideus, Proc. Gen. Fish. Council Medit. vol. 6, p. 203, 1962. Water Poll. Abs., vol. 35, p. 2407.
- 78. Maldura, C. "Action of Alkyl Aryl Sulfonate on Salmo gairdnerii."
 Gen. Fish. Council Medit. Proc. Tech. Papers, vol. 6, p. 203, 1961.
- 79. Malina, J. F. Jr., "Toxicity of Petrochemicals in the Aquatic Environment," Water and Sew. Wks., 111(10), pp. 456-460, 1954.
- 80. Mann, H. "Increase by Detergents of Effects on Taste in Fish,"

 Fischwirt, vol. 12. pp. 237-240. 1962. Liber. Wass. Abwass. Luft

 u. Boden, 63(11), p. 122. 1962. Water Poll. Abs., 37(6). Abst. No. 1001. 1964.
- 81. Mann. H. "The Importance of Synthetic Washing Agents (detergents) to Fisheries," Fischwirt, vol. 12, pp. 97-101, 1932, LitBer Wass.

 Abwass, Luft. u. Boden, vol. 11, p. 123, 1962/63, Water Poll. Abs., (Brit.), vol. 37, p. 1010, 1964.
- 82. Mann, H. "Effects on the Flavor of Fishes by Oils and Phenols."

 Pollutions Marines par les Microorganismes et les Produits Petroliers."

 Comm. Intl. Pour L'Exploration Scientifique de la mer Mediterrance.

 Symposium de Monaco, p. 371-374. April 1984.
- 83. Mann, H., and O. J. Schmid. "Die emfluss von detergentien auf sperma, befruchtung and entwicklung bei der forelle," Int. Rev. Ges. Hydrobiol., vol. 46, p. 419, 1961.
- 84. Mann, H. and O. J. Schmid. "Der einfluss subletaler mengen von detergentien (Tetrapropylenbenzolsulfonat) auf das Wachstum von Lebistes Reticulatus," Arch. Fischwiss, (Germany) 16(1), pp. 16-20, 1965.
- 85, Marchetti, R. "The Toxicity of Nonyl Phenol Ethoxylate to the Developmental Stages of the Rainbow Trout, Salmo gairdnerii, Richardson," Ann. Appl. Biol. (Brit.), vol. 55, pp. 425-430, 1965. Biol. Abs., vol. 46, p. 87520,
- 86. Marchetti, R. "Studies on the Toxicity of Some Surfactants to Fishes." Riv ital. Sost grasse, vol. 41, pp. 533-542, 1964, J. Am. Oil Chem. Soc., vol. 42, p. 390A, 1965.
- 87. McCauley, R. N. "The Biological Effects of Oil Pollution in a River," Limnology and Oceanog., vol. 11, no. 4, pp. 475-486. October, 1966.

- 88. Menzel, R. W. Report on Two Cases of Oily Tasting Oysters at Bay Sainte Elaine Oilfield, Texas A&M Res. Foundation Project 9, Unpubl. Rept., 9 pp. 1948.
- Menzel, R. W. and Hopkins, S. H. Report on Commercial-Scale Oyster Planting Experiments in Bayon Bas Bleu and in Sainte Elaine Oil Field, Texas A&M, Project 3 Rept., 148 pp. plus 61 fig. 1952.
- 90. Menzel, R. W. and Hopkins, S. H. Report on Experiments to Test the Effects of Oil Well Brine or Breedwater on Oysters at Lake Barre Oil Field, vol. II, 126 pp. (mimeo). September 11, 1951.
- 91. Nehring, D. "Laundry Waste Waters and Fish," Disch. FichZig, vol 9, p. 46. 1962. LitBer, Wass, Abwass, Luft u. Boden, vol. 11, p. 37. Water Poll. Abs., (Brit.), vol. 37, p. 186. 1964
- 92. Nehring, D. "The Action of Flotation Reagents on Fish and Fishfood Animals," Z. Fischerei 11(3/4), p. 313. Chem. Abs., vol. 60, p. 7204. 1964.
- 93. Nelson-Smith, A. "The Effects of Oil Pollution and Emulsifier Cleansing on Shore Life in South-West Britain," <u>Jour. Applied Ecology</u>, 4(2). 1967.
- 94. Nelson-Smith, A. "Conservation and the TORREY CANYON: Oil, Emulsifiers, and Marine Life," J. Devon Trust for Nature Conservation (Suppl.), pp. 29-33. 1967.
- 95. Niemitz, W. and Pestlin, W. "The Effect of Biological Sewage Treatment on the Harmfulness of Detergents to Fish," Stadtehygiene, vol. 13, pp. 231-233, 1962. Water Poll, Abs., (Brit.), vol. 37, p. 863, 1964.
- 96. Nitta, T., K. Arakawa, K. Okubo, T. Okubo and K. Tabata. "Studies on the Problems of Offensive Odors in Fish Caused by Wastes from Petroleum Industries," <u>Bull. Tokai Reg. Fish. Res. Lab.</u>, no. 42, 23 (Japanese with English summary). 1965.
- 97. North, W. J., Neushul, Jr., M. and Clendenning, K. A. "Successive Biological Changes Observed in a Marine Cove Exposed to a Large Spillage of Mineral Oil," Pollutions Marines par les Microorganismes Scientifique de la mer Mediterranee, Symposium de Monaco, pp. 335-354. April 1964.
- 98. North, W. J. "TAMPICO a Study of Destruction and Restoration." Sea Frontiers, vol. 13, pp. 212-217, 1967.
- 99. Oglesby, R. T. and Sylvester, R. O. "Marine Biological Monitoring of Oil Refinery Liquified Waste Emissions," Proc 19th Ind. Waste Conf. Purdue Univ., Engng, Extn. Ser. No. 117, pp. 167-179, 1964, Water Poll. Abs. (Brit.), vol. 39, p. 339, 1986.

- 100. O'Sullivan, A. J. and A. J. Richardson. "The TORREY CANYON Disaster and Intertidal Marine Life," Nature, vol. 214, pp. 448-542. 1967.
- 101. Pauley, G. B., K. K. Chew, and A. K. Sparks. "Experimental Infection of Oysters (<u>Crassostrea gigas</u>) with Thigmotrichid Ciliates," J. Invertebrate Pathol., vol. 9, pp. 230-234. 1967.
- 102. Phillips, A. H. Effects of Oil Refinery and Domestic Sewage Effluents on Fish Populations of a Southwestern Stream, Oklahoma State Univ. Master of Science Thesis, 27 pp. 1963.
- 103. Pickering, Q. H. and Henderson, Croswell. "Acute Toxicity of Some Important Petrochemicals to Fish. J. Water Poll. Cont. Fed., vol. 38(9), pp. 1419-1428. 1966.
- 104. Pickering, Q. H. "Acute Toxicity of Alkyl Benzene Sulfonate and Linear Alkylate Sulfonate to the Eggs of the Fathead Minnow, Pimephales Promelas," Air and Water Pollut. Int. J., vol. 10, pp. 385-391, 1966.
- 105. Reichenback-Klinke, H. "Auswirkung von ol-und Teerprodukten im Wasser auf den Fischorganismus," Munchner Beitrate Zur Adwasser-, Fischerei-und Flussiologie, vol. 9, p. 73. 1962.
- 106. Reichenback-Klinke, H. H. "Intiofauna Dunarii in raport cu incarcarea cu deversari," <u>Hidrobiologia</u>, vol. 217-222 (Romanian with German summary). 1964.
- 107. Reichenback-Klinke, H. H. "The Phenol Content of Water in its Effects on the Fish Organism," Arch. Fisch-Wiss. (Germany), vol. 16, p. 1. 1965.
- 108. Reiman, K. "Die schadlichkeit von detergentien fur wasser organismen," Munchener Beitrage zur Abwasser-, Fischeriei-, und Fluss-biologie, vol. 9, p. 206. 1962.
- 109. Russell, F. E. and P. Kotin. "Squamouns papilloma in the White Croaker," J. Nat. Cancer Inst., vol. 18, pp. 857-861, 1956.
- 110. Reimann, K. "Harmfulness of Detergents for Water Organisms,"

 Munch. Beitr. Abwass. Fisch. -u. FlussBiol., vol. 9, pp. 206-214.

 LitBer. Wass. Abwass. Luft u. Boden, vol. 11, pp. 197-198. 1962/33.

 Water Poll. Abs., (Brit.), vol. 37, p. 1377. 1964.
- 111. Reimann, K. "Harmfulness of Oil and Tar Products to Lower Water Organisms," Munch. Beitr. Abwass. -, Fisch. -u. FlussBiol., vol. 9, pp. 60-72. 1962. LitBer. Wass. Abwass. Lujt u. Boden, vol. 11, p. 194. 1962/63. Water Poll. Abs., (Brit.), vol. 37, p. 1375. 1964.

- 112. Reish, D. J. The Effect of Oil Refinery Wastes on Benchie Marine Animals in Los Angeles Harbor, California. Pollutions Marines par les Microorganismes et les Produits Petroliers. Comm. Intl. Pour L'Exploration Scientifique de la mer Mediterrance. Symposium de Monaco, p. 355-61. April 1964.
- 113. Schafer, R. D. "Effects of Pollution on the Free Amino Acid Content of Two Marine Invertebrates," Pacific Sci., vol. 15, pp. 49-55, 1961.
- 114. Schafer, R. D. "Effects of Pollution of the Amino Acid Content of Mytilus edulis," Pacific Sci., vol. 17, pp. 246-250, 1963,
- 115. Scheler, A. and Cairns, Jr., J. "Persistence of Gill Damage in Lepomis Gibbosus Following a Brief Exposure to Alkyl Benzene Sulfonate," <u>Notulae Naturae</u>, no. 391, 7 pp. 1986.
- 116. Schinezel, A. and H. Benger. "The Danger to Surface Waters from Transport of Phenol," Zentbl. Bakt. Paraisit Kde, I. Ref. 201, pp. 339-340, 1966.
- 117. Schmid, O. J. and H. Mann. "Action of a Detergent (Dodecylbenzene sulphonate) on the Gills of the Trout," Nature, 192(4803), p. 675. 1961.
- 118. Schmid, O. J. and H. Mann. "Die Einwirkung von Dodecylbenzolsulfonat auf die Kiemen von Forellen," <u>Archiv. für Fischereiwissenschaft, Heft</u> 1/2, pp. 41-51, (13 Jahrgang). 1962.
- 119. Schaut, G. G. "Fish Catastrophes During Drought," Jour. Am. Water Works Assn., vol. 31, p. 771. 1939.
- 120. Schulze, E. "The Effect of Waste Waters Containing Phenol on the Taste of Fish," Int. Rev. Hydrobiol., vol. 46, pp. 419-426, 1961.

 LitBer. Wass. Abwass. Luft u. Boden, vol. 11, p. 40, 1962. Water Poll. Abs., 37(1), Abst. No. 182, 1934.
- 121. Shimkin, M. B., B. K. Koe, and L. Zechmeister. "Instance of Occurrence of Carcinogenic Substances in Certain Barnacles," Science, vol. 113, p. 650, 1951.
- 122. Shaw, J. M. and F. L. Timmons. Controlling Submersed Water Weeds on Irrigation Systems with Aromatic Solvents. U. S. Bur. Reclamation and U. S. D. A. Joint Rept. 1949.
- 123. Silverling, Bill. "Oil Brings Disaster to Beach Life." Seattle Post-Intelligencer. March 18, 1964.
- 124. Simpson, A. C. <u>TORREY CANYON Interim Report on Fishery Aspects</u>. Fish. Lab., Burnham-on-Crouch, Essex, England, Unpubl. (mimeo). Rept. 8 pp. 1967.

- 125. Skrapek, K. Toxicity of Phenols and Their Detection in Fish. Ustav ved, inform. Min. Zemed., Lesn. Vod. Hospod. Air. Vyr., vol. 8 pp. 499-504, 1963. Water Poll. Abs. (Brit.), vol. 39, p. 1411. 1966.
- 126. Snow, C. Dale. "Oil Pollution; Yaquina Bay," Unpubl. Memorandum. Oregon Fish Commission, 4 pp. 1963.
- 127. Sparks. A. K. and G. B. Pauley. "Studies of the Normal Postmortem Changes in the Oyster, Crassostrea Gigas (Thunberg)." J. Insect Patho., 6(1), pp. 78-101, 1964.
- 128. Sugimoto, H. M. Suzuki, and O. Takeuchi. "Studies of the Oil Pollution on the Fishing Ground in Seto Island Sea. I Distribution of Oily Wastes in the Sea," <u>Bull. of the Jap. Soc. of Sci. Fish</u>, 30(7), pp. 542-554. 1964.
- 129. Surber, E. W., J. N. English, and G. N. McDermott. "Tainting of Fish by Outboard Motor Exhaust Wastes as Related to Gas and Oil Consumption," Biological Problems in Water Pollution, Third Seminar, U. S. Public Health Service, Cincinnati, Ohio, pp. 170-173. 1952.
- 130. Surber, E. W., and Thatcher, T. O. "Laboratory Studies of the Effects of Alkyl Benzene Sulfonate (ABS) on Aquatic Invertebrates," <u>Trans. Amer. Fish. Soc.</u>, vol. 92, pp. 152-179, 1963.
- 131. Sollman, T. "Correlation of the Aquarium Goldfish Toxicities of Some Phenols, Quinones, and Other Benzene Derivatives with Their Inhibition of Auto-Oxidative Reactions," <u>Jour. Gen. Physiology</u>, vol. 32, p. 371, 1949.
- 132. Swisher, R. D., J. T. O'Rourke and H. D. Tomlinson. "Fish Bioassays of Linear Alkylate Sulfonates (I-AS) and Intermediate Biogradation Products," J. Amer. Oil. Chem. Soc., vol. 41, pp. 746-752, 1954.
- 133. Tagatz, M. E. "Reduced Oxygen Tolerance and Toxicity of Petroleum Products to Juvenile American Shad," <u>Chesapeake Sci.</u>, 2(1-2), p. 65-71, 1961.
- 134. Tegelberg, H. "Washington's Razor Clam Fisheries in 1934," Ws. State Dept. Fisheries 74th Ann. Rept., p. 53-56, 1964,
- 135. Tendron, G. "La Pollution des mers par les Hydrocarbures et la Contamination de la Flore et de la Faune Marines," <u>Penn. Ar. Bed.</u>, vol. 3, pp. 178-191, 1962.
- 136. Thatcher, T. O. "The Comparative Lethal Toxicity of a Mixture of Hard ABS Detergent Products to Eleven Species of Fishes." Air and Wat, Pollut. Int. J., vol. 10, pp. 585-590, 1969.

- 137. Turnbull, H., DeMann, J. G. and Weston, R. F. Poxicity of Various Refinery Materials to Fresh Water Fish. Ind. and Eng. Chem., vol. 46. pp. 324-333, 1954.
- 138. Vernidub, M. F. "The Effect of Drainage Water of the Gas-Shale Industry on the Physiological Processes and Growth of Larvae and Young Salmon," Biol. Abs., vol. 43, no. 3, Abst. No. 8764, 1963.
- 139. Vernidub, M. F. "Experimental Analysis of Processes Caused by Poisoning with Non-volatile Phenols in Baltic Salmon in the Larval Period," Biol. Abst. vol. 45, no. 20, Abst. No. 85148. 1964.
- 140. Vishnevetskii, F. E. "The Pathological Morphology of the Peisoning of Fish by Phenol and Watersoluble Components of Crude Oil, Coal Tar and Fuel Oil," Trud. Asktrankhan Gos. Zapoved., vol. 5, p. 350. 1962. Biol. Bas., vol. 42, p. 1026. 1963. Water Poll. Abs., (Brit.) vol. 37, p. 183. 1964.
- 141. Waluga, D. "Phenol Effects on the Anatomico-Histo-Pathological Changes in Bream (Abramis brama L.)," Acta Hydrobiol., 8(1), p. 55-78. 1966.
- 142. Waluga, D. "Phenol Induced Changes in the Peripheral Blood of the Breams Abramis brama (1.)," Acta Hydrobiol., 8(2), pp. 87-95. 1966.
- 143. Ward, C. K. and Irwin, W. M. "The Relative Resistance of Thirteen Species of Fishes to Petroleum Refinery Effluent," Proc. Fifteenth Ann. Conf. Southeastern Assoc. Game Fish. Comm., p. 255. 1961.
- 144. Wiebe, A. H. "The Effect of Crude Oil on Fresh-Water Fish." Trans. Amer. Fish. Soc., vol. 65, pp. 324-331. 1935.
- 145. Wallen, I. E. A Bio-Assay Evaluation of Certain Oil Refinery Wastes for their Toxicities to Fishes in the Presence of Turbidity Due to Clay and Silt. Unpubl. Research, Okla. A&M College. 1955.
- 146. Wunder, W. "Schadigung von eisommerig Karpfen im Winterteich durch Olabwasser," I. Teil: Anfangerscheinungen am Fischkorper. Allg. Fischerei Zeitung. 99(22), pp. 673-674. 1964.
- 147. Wurtz-Arlet, J. "Laboratory Study of the Toxicity of Certain Synthetic Detergents to the Rainbow Trout," Vortaege Originalfassung Intern. Kongr. Grenzflaechenaktive Stoffe, 3, Cologne, vol. 3, p. 329, 1960, Chem. Abs., vol. 57, p. 10374, 1962.
- 148. Young, P. H. "Some Effects of Sewer Effluent on Marine Life." Calif. Fish and Game, vol. 50, pp. 33-41, 1964.
- 149. Zahner, R. "The Effect of Motor Fuels and Oils on Rainbow Trout," Vom Wasser, vol. 19, pp. 142-177, 1962. Water Poll, Abs., 37(6), Abst. No. 1017, 1964.

150. ZoBell, C. E. "The Occurrence, Effects, and Fate of Oil Polluting the Sea, Internati. Conf. Water Poll. Res. Lordon, pp. 85-118, 1964.

Addenda

- 151. Alyakunskaya, I. O. "Behavior and Filtering Ability of the Black Sea Mussel Mytilius galloprovincialls, on Oil Polluted Water," ZOOH Zh, vol. 95, pp. 998-1003. 1966. Bio. Abstracts, vol. 48, p. 6494. 1967
- 152. Calabrese, A. and H. C. Davis. "Effects of 'Soft' Detergents on Embryos and Larvea of the American Oyster (Crassestrea virginica)," Proc. Natl. Shellfish Assoc., vol. 57, pp. 11-18, 1987.

8.2 OIL POLLUTION AND WATERFOWL

Introduction

1

Contamination of migratory birds in coastal and inland waters by floating oil is one of the most spectacular and notable results of petroleum pollution in aquatic environs. In instances of major disasters such as wrecked oil tankers, public response is usually instanta, fous because of extensive coverage in newspapers and descriptive accounts in ornithological journals. Dead or moribund birds covered with oil accumulate along shorelines and are found by people in the course of daily routine or recreational activities. At this time, most published reports concerned with the effects of oil and oily wastes on birds deal with localized and immediate mortalities. In very few cases, such as Tuck, (80) have either the short or long term effects of oil on bird populations been accurately evaluated and defined.

The most comprehensive review dealing with the existing interrelationships between waterfowl and oil is presented by Erickson; (28) much of the generalized material in the two subsequent sections is from this article. Restoration of waterfowl is discussed in Section 3.3.3.

Scope of the Problem

Oil pollution of the sea did not become a major problem until World War I when fuel oil came into widespread use, although there has always been some natural release of petroleum from submarine and shoreline oil deposits. Increased domestic use of oil has resulted in a corresponding increase in the need for storage and transportation. Birds did not become radically involved in the problem until the 1930's. The status of oil pollution on the coast of the United States and its relation to waterfowl in early years is discussed by Lincoln. (57) Sources of oil pollution at sea are reviewed by Hawkes, (43) who stated that the principal source is now shipping. Oil is dispersed from ships when they refuel, pump bilges, and wash tanks. Much oil is lost through leaking hulls. Shipping accidents such as grounding cause disasterous spills of oil, and losses from oil-drilling and natural seepage are less important. Sinkage of ships during both World Wars contributes to the problem, as oil may leak from sunken hulls for extended periods of time.

Frickson (28) stated that, "Nearly every body of water on earth, fresh or salt, is occupied by migratory birds at one time or another. The potential for losses of waterfowl thus exists almost everywhere that surface waters are contaminated by oil. In North America, greatest losses of migratory birds to oil pollution have been observed along the coast and in offshore waters of the Atlantic Ocean and, to a lesser extent, the Gulf of Mexico and Pacific Ocean. Losses have been particularly heavy in or adjacent to the principal harbors and oil refineries of the northeast and along the more heavily travelled shipping lanes. The problem has also been encountered in various inland waterways including the Great Lakes." Another focal point is the coast of Newfoundland, where oil pollution is considered to originate from ships using heavily travelled North Atlantic routes. (32) British law strictly forbids the dumping of oil in areas where ocean currents carry oil to the vicinity of England. One of these zones extends westward to the longitude of Greenland and another includes the whole of the North Sea.

As summarized by Erickson, (28) "Oil contamination in habitats utilized by migratory birds may be determined at any time of the year. Losses may occur during the colder months when greatest numbers of birds are present, or during the growing season when oil may blanket the shores or bottom and reduce or eliminate important sources of food. It is the oil spillage during the seasons and in the areas of heavy migratory bird use that brings about the spectacular losses reported in the press. Because spillage often occurs in or near human population centers along the coast, especially in bays or harbors, losses to coastal dwelling wildlife are much more likely to be observed than mortality of offshore dwellers that come into contact with oil out at sea and die unnoticed. Birds that are year-around residents along the coast would appear to be highly vulnerable, for they must survive a much greater period of direct exposure to oil each year than those that appear briefly as migrants."

Moreover, "It is extremely difficult to assess the importance of oil-caused mortality in most wildlife populations. This is particularly true with the very mobile forms. Movements of population units through a contaminated location and various other factors make it difficult to measure

what proportion of the total population has come in centact with oil, and, of the segment that has, what proportion is lost, "(28) It is possible, however, to assess direct mortality from living birds provided that accurate estimates of population abundance are available immediately preceding a disaster, and that a similar estimate is made when the oil has disappeared. These estimates hold greatest reliability when the population is relatively stationary, as in case of rookeries during breeding seasons. Estimates of mortality, although not as statistically reliable, can also be made when population trends are known for a given area over a number of years. However, many other mortality factors face migratory birds, especially those species that must survive semiannual flights and an annual hunting season. Oil pollution is not necessarily the cause of annual fluctuations in population levels of waterfowl.

It is the general consensus that relatively few of the birds that contact oil and die far out at sea are found. Hawkes (43) believed that the slow. steady kill of sea birds as a result of bilge pumping and tank washing may, in the long run, account for more losses than publicized ship disasters. The proportion of birds that ultimately drifts to the coast and is seen depends upon air and water currents, the period during which carcasses remain afloat and on the beach, frequency of surveillance of drift materials, and other factors. (28) Therefore, estimates of mortality based on observed remains of oil-soaked waterfowl ordinarily have value only as minimal indications of loss because the clements that singularly or in combination operate to obliterate the evidence may be extremely varied in their ultimate effects. Because many other mortality factors face migratory birds. especially those species that must survive semiannual flights and the annual hunting season, the importance of pollution-caused mortality in the overall scheme of management and preservation of some species is difficult if not impossible to assess accurately, (28)

Nature is concerned not so much with the survival of an individual, but with perpetuation of the species. Erickson⁽²⁸⁾ believed that, "Wide dispersal of a bird population at the time oil is discharged upon the water may spread the risk and be safer than concentration of the entire group in an exposed but limited location."

It has been stated and frequently repeated that "a spot of oil the size of a quarter on the breast of a bird is sufficient to cause death." However, it cannot be assumed that all waterfowl coming in contact with oil are doomed. The number of birds that survive may be considerably larger than the number that die. (28) Hunters are reported to have encountered "oilburn" on bagge lucks, and oil contamination has been noted on plumage of ducks shot for sport. Many hunters are reluctant to use oil-stained birds for food and discard them because of actual or imagined tainting of flesh. Because oil is often ingested in the process of preening, palatability of contaminated ducks may be reduced, particularly if the birds are not dressed soon after being shot. Furthermore, if the feeding activities of birds have been hampered because of oil, they may be in poor flesh and less desirable for the table. (28)

Effects of Oil on Waterfowl

Large numbers and many species of waterfowl are involved in the oil pollution problem. Most, if not all of the migrants that alight on the open sea, that feed or rest in coastal bays or estuaries and on inland waters, or that move up and down the beach are subject to contamination. Birds on the sea acquire oil on their plumage from the many sources of oil along the coasts. In inland waters, birds become oiled from borrow pits adjacent to freshly surfaced highways, from polluted ponds associated with oil processing, from accidental spills in inland waterways, and from accumulated deposits originating from industrial plants. (28)

The possibility has been suggested that birds such as ducks or gulls are attracted to oil slicks on surrounding choppy waters because the calm surface may falsely indicate the presence of submerged vegetation or shoals of fish. (45, 79) It has yet to be demonstrated that waterfowl are actually attracted to oil, and it may be that contamination of birds occurs when they simply use the oiled areas for routine activities such as feeding and resting.

Numerous accounts list the species of waterfowl found as casualties of oil pollution. Virtually all seabirds are affected. * Although there is considerable variation depending on the number and species normally present in different areas, and on the season of their occurrence and abundance, there is a general relationship between the amount of time a species apends in the water and frequency of contamination. Erickson (28) lists two contrasting examples: 1) murres which spend most of their time in the water while not nesting and are subject to extensive losses, and 2) gulls which are extremely abundant in harbors and other coastal areas subject to oil spillage and seem to suffer less damage. The implication is that gulls spend much of their time away from the water or in shallows where their feet, rather than their plumage, are more likely to come into contact with oil, (65) and they are able to regargitate ingested material. However, some observers feel gulls are inherently more capable of withstanding actual fouling by oil than are most types of migratory birds. (28) Many species of waterfowl tainted by floating oil on open water attempt to swim to the nearest land where they wander ashore and seek sanctuary, sometimes in freshwater ponds. (22, 45, 72, 69, 78)

Oil is, potentially, of greatest danger to waterfowl when adults and young are flightless on the water during prolonged periods of moult such as frequently occurs during late summer.

Erickson (28) pointed out that the effects of oil on birds depend upon a variety of factors including the type of oil, extent of contamination of plumage, temperature of the air and water, and probably the quantity of oil ingested. The heavier oils appear to represent a greater problem than the more volatile and readily dispersed types. The effects of oil on sea birds may be briefly summarized as follows: (43, 57, 72, 74)

- 1. The oil sticks and coagulates, so that the bird cannot remove it.
- 2. The oil destroys natural bouyancy, so that the bird extends greater effort to remain affoat.

^{*}The birds most commonly associated with oil pollution include aaks, auklets, dovekies, eiders, scoters, gannets, grebes, guillemots (or murres), scaup ducks, oldsquaw ducks, goldeneye ducks, various gulls, loons, murrelets, shearwaters, fulmars, petrels, puffins, terns, and curlews. Even geese and swans have been effected on occasion.

- 3. The oil destroys natural insulation, so that the bird is exposed to chilling air and water temperatures.
- 4. The oil matts the feathers, so that the bird cannot fly.
- 5. The oil, under the above conditions, prevents the bird from obtaining food.
- 6. Some oil, sometimes toxic, is swallowed when the bird attempts to preen.

Consequently, an oiled bird suffers from exhaustion, exposure, starvation, and sickness. Survival under such conditions is difficult and very problematical.*

Early accounts indicate that the digestive tract of birds became lined with oil residue and that the weight or flesh of the victims was below normal. The assumption was that ingestion of oil in many cases proved fatal. Recent studies provide additional information on the toxic effects of oil ingested by waterfowl. Hunt (49) reported that three ducks experimentally exposed to an aromatic oil died, apparently due to the toxic properties of the oil. Recent studies by Hartung, (38, 40, 41) using oil labelled with radioactive traces, showed that oiled ducks ingest significant quantities of oil in preening their plumage. Hartung and Hunt (37) found that ingestion of industrial oils by ducks causes lipid pneumonia, gastrointestinal irritation, fatty livers, and adrenal cortical hyperplasia; cutting oil and diesel oil results in acinar atrophy of the pancreas; -diesel oil and fuel oil sometimes produce toxic nephrosis. (37) Relatively nontoxic lubricating oil causes ducks to cease laying, and small quantities of the oil on duck eggs reduces hatchability. (39) Rittinghaus (73) stated that eggs of a Cabot's tern that received oil from the plumage of the female did not hatch.

As noted by Erickson, ⁽²⁸⁾ "Migratory birds are indirectly affected by deposits of oil on the bottom in shallow water or along the shore that reduce the available food supply of both plant and animal matter. Various elements in food chains are eliminated by chemical or physical properties of the oil, or items in the diet of waterfowl may become unavailable by being overlaid or imbedded in tarry materials. The use of important feeding

^{*}Oil may also effect aquatic mammals although, in contrast to waterfowl fewer records are available. These animals include muskrats, (13, 66, 86), beavers, (66) fur seals, (8, 88) and even deer. (66) Fuel oil rapidly destroys the water proof qualities of muskrat furs. (86)

grounds has declined greatly after pollution by oil, either because of the elimination of essential food and cover, or because fouling of the habitat has reduced the attractiveness of the areas. Shorebirds that rely upon intertidal zones for their feeding grounds may find them completely covered with oil." Accumulation of petroleum sludge on the bottom may also prevent germination and growth of plants and the production of invertebrates important as food, either by smothering or by toxic effects.

Review of the Literature

For convenience, the literature is listed categorically by general area subjected to oil pollution. Although extensive, the literature covered herein cannot be construed as complete.

General Presentations. The most recent and comprehensive reviews of the existing relationships between oil and waterfowl are given by Erickson. (28, 29)

An early discussion concerning the effect of oil pollution on marine and wildlife is provided by Lane et al. (54) General accounts of oil pollution of the sea, its sources, affects, and existing legisliation, are provided by Lincoln, (57) Adams, (1) Galtsoff, (31) Giles and Livingston, (32) Callaghan, (23) Hawkes, (43) Barclay-Smith, (87) and Gonder. (33) Hunt (47) reviews the direct effects of pollution, including oil, on plants and animals in the Great Lakes.

Floating oil as a hazard to seabirds along the coast of Europe was discussed by Ringleben, ⁽⁷¹⁾ Taning, ⁽⁷⁶⁾ and Brouwer. ⁽¹⁸⁾ Beauty ⁽¹³⁾ sent questionnaires to 48 states, and reviewed the existing status of oil pollution and wildlife in 1948 on the basis of 24 replys. Livingston ⁽⁶⁰⁾ reviewed the slaughter of seabirds by oil. Barclay-Smith, ^(9, 10, 11, 12) discussed oil pollution of the sea with particular reference to England, measures taken to prevent oil pollution, and British contributions to bird protection.

Results of a panel discussion at the 52nd Annual Convention of the National Audubon Society concerning the menace of oil pollution are presented by the Audubon Editor. (8) Several reports dealing with the effects

of oil pollution on scabirds were given at the 1959 International Conference on Oil Pollution of the Sea at Copenhagen, including papers by Brown, (19) Bruijns, (21) Tuck and Livingston, (81) and Angus. (3) Dennis (26) reviews the question, "Can oil pollution be defeated?," in an optimistic vein.

Anonymous short accounts of deaths of scabirds from oil are numerous, particularly in recent years. (5, 6, 7) Livingston considered that the toll of scabirds from oil in 1960 was the most extensive to date.

Atlantic Coast of the United States. Destruction of sea birds from the grounding of the steamer E. LUBINBACK in Long Island Sound in 1930 was described by Hadley. (35) Although some oil was initially lost from smashed tanks, thousands of gallons were pumped overboard during salvage operations with disasterous consequences.

Conditions associated with oil pollution off the coast of Massachusetts in February 1942, were described by Ripley. (72) who believed that most of the oil then originated from ships sunk during the World War II. Peterson also reviewed reports of oil-affected birds along the northeastern coast of North America in 1942 after the U.S. entered World War II. Peterson believed that the most damage occurred in winter flocks and that after April, when populations had dispersed northward, the losses decreased even though tanker sinkings continued.

According to Burnett and Snyder, (22) a February storm in 1952 caused the breakup of two sunken tankers off Chatham, Massachusetts, and 150,000 barrels of oil were released. Eiders wintering at the Monomoy National Wildlife Refuge were severely affected; the estimated population of 500,000 wintering eiders in 1952 had decreased to 150,000 birds in 1953. Dennis (27) records that an estimated 7500 birds perished on the beaches of Nantucket, off Massachusetts, during the winter of 1956. The common eider, which winters there in large concentrations, accounted for 80% of the total. Dennis also commented, "Apparently all that is required is a patch of oil about 1 in. in diameter to break down the insulation of the plumage and expose the bird to cold and p neumonia."

The Pacific Coast of the United States. On March 6, 1937, the oil tanker FRANK H. BUCK, carrying 2,730,000 gal, of crude oil, was struck by a passenger steamer and became stranded offshore of Golden Gate, San Francisco Bay, California. Aldrich⁽²⁾ reviewed the species of water birds affected by the released oil. According to Mofitt and Orr, ⁽⁶⁵⁾ little oil entered San Francisco Bay, but the oil contaminated 55 miles of shoreline and upwards of 10,000 birds perished. Among the offshore species, California murres suffered the greatest mortalities and the accident may have inflicted serious losses among nesting colonies. Houldson⁽⁴⁶⁾ reviewed the relationships between oil and populations of murres off California.

On September 6, 1956, the freighter SEAGATE ran aground near Point Grenville on the west side of the Olympic Peninsula, Washington. Broken fuel tanks spread oil over the surrounding sea. Richardson surveyed the area and found that dead white-winged scoters averaged 132, 5 birds per mile, while oil-contaminated common murres averaged 56, 5 birds per mile.

A barge carrying an excess of 2, 300, 000 gal. of petroleum products grounded off Moclips, Washington, on March 11, 1964. According to Lindsay and Tegelberg, ⁽⁵⁸⁾ oil was released from weakened seams and later pumped overboard. Although numerous gulls were present along the contaminated shore, few appeared to be affected; contamination of other species was not reported.

The Atlantic Coast of Europe. Bruijns (20, 21) made a census of sea birds falling victims to oil pollution along the 400 km coastline of the Netherlands from 1948 to 1958. Scoter ducks composed 41% of the birds found and 18% guillemots; most oiled birds were found during the winter found and 18% were guillemots; most oiled birds were found during the winter from December to March. Bruijns estimated a minimum of 20,000 -- and perhaps as many as 50,000 -- birds were contaminated each year. Similar of birds affected since 1948-1958 was indicated. The decline was not ascribed to a lessening of oil pollution, but to better diagnosis, fewer catastrophies, and different direction of the prevailing winds. They estimated that at least 11,000 birds killed by oil accumulate annually along Netherland shores.

Rittinghouse⁽⁷³⁾ reported an incident in which Cabot's terms and other shorebirds acquired oil and washed ashore at a bird sanctuary. Other waterfowl were depicted as victims of oil pollution in Europe by Ticehurst, ⁽⁷⁸⁾ Martini, ⁽⁶¹⁾ Henneberg, ⁽⁴⁴⁾ Ridder, ⁽⁷⁰⁾ Bergstrom, ⁽¹⁴⁾ Kuchler, ⁽⁵³⁾ and Hautekiet. ⁽⁴²⁾ Grenquist⁽³⁴⁾ discussed examples of damage to waterfowl in the vicinity of Finland. Oil Pollution on the coast near Gretford, Sweden was believed to have killed 30,000 seabirds. ⁽⁸⁾ The effect of two oil spills in Poole Harbor, England on water birds was evaluated by Ranwell and Hewett, ⁽⁶⁸⁾ The first spill was a minor release from a land installation, the second was a collision between two ships which released 61,000 gal. of oil. At least 300 birds of 32 species were known to be affected. Harrison reports on the birds destroyed by 1700 tons of oil accidentally pumped from a German tanker into the Medway River, England.

The effects of oil on birds resulting from the wreck of the TORREY CANYON off England on March 18, 1967 was reviewed by Spencer. (75) By April 17, 7849 birds had been collected of which 2030 were dead or moribund on arrival at cleaning stations. Of these, 6355 were guillemots and 1384 were razorbill auks. The minimum number of birds known to be affected was 10,000 but the upper limits could only be postulated. The actions taken by the Royal Society for the Protection of Birds after the TORREY CANYON disaster were summarized by Merrin and Jackson. (62) Bourne, Parrick, and Potts (15) report that the TORREY CANYON disaster probably killed more t. n 30,000 seabirds. Ninety-eight percent of the kill were guillemots and razorbills, and involved local British populations of adults birds; a disproportionately high number of the more migratory young birds was found. Williams (84) and Spooner (88) believed that, in addition to the oil, a high proportion of the birds recovered after the TORREY CANYON suffered from detergents used in cleaning operations on the coast of Britain.

According to Manwell and Baker, ⁽⁸⁹⁾ one authority attributes the marked decline in the last thirty years of certain species of diving birds (e.g. guillemots, razorbills, and possibly puffins) in the British Isles as being due largely to repeated oil pollution.

Atlantic Coast of Canada and Newfoundland. Informal reports concerning damage to waterfowl along the coast of Nova Scotia were furnished by Tufts (82,83) and by Boyer. (16,17) Horwood (45) published an informal account of sea-birds affected by oil off Newfoundland. He considered the major source of oil to be bunker and oil tankers which dumped oil wastes in shipping lanes. Hawkes (43) relates that one colony of auks estimated at 250,000 birds nesting on the Newfoundland coast was nearly decimated by oil during a two-year period.

Intensive studies on the effects of oil on Newfoundland sea birds were reported by Tuck and Livingston (81) and Tuck. (79) Oil pollution off the eastern coast of Newfoundland first became serious in 1935, and in each year since 1950 there have been excessive mortalities. The kill in 1960, where several hundred thousand birds died from January to March, exceeded that of any recorded year. Tuck (79) noted that the Laborador current meets the Gulf Stream off the southeast edge of the Grand Banks, and ocean going vessels converge at this point. Tuck indicated that as long as oil is dumped or spilled in a region extending 300 miles off the east coast of Newfoundland, pollution of beaches and a high mortality of sea birds is inevitable. High mortalities in winter and spring are correlated with large concentrations of wintering or breeding birds and prevailing easterly winds that drift oil shoreward. Tuck (80) reviews the effects of oil pollution on migratory birds off Newfoundland, with particular reference of extensive damage to murres.

Great Lakes Area of the United States. Losses of waterfowl from oil contamination is not confined to coastal areas. The Great Lakes area of the United States and Canada, as well as surrounding regions where oil spills have occurred, provide well-documented examples. According to Dennis, (25) every one of the Great Lakes has been subject to oil spills and slugs of oil. Miller and Whitlock (64) estimated 10,000 ducks perished in the Detroit River, Michigan, but attributed the loss of birds to a combination of cold weather, lack of food, and industrial pollution. A survey team of the International Joint Commission (52) later estimated than 16,000 gal, of

oil were entering the Detroit River daily in the years 1946-48, and reported that dredging of the lower three miles of the Rouge River, a tributary of the Detroit, scooped more than 17,000 gal. of oil and grease from the bottom each day for a period of 50 days.

Hunt and Ewing⁽⁵¹⁾ investigated mortalities of waterfowl in the Detroit River and concluded that oils and greases were among the factors most harmful. Studies by Hunt^(48, 49) provided additional data on the effects of oil pollution on ducks using the Detroit River. Hunt and Cowan⁽⁵⁰⁾ reported that 10,000 to 12,000 ducks died in the Detroit River during the winter of 1960, and believed that a large majority, if not all, of the dead aucks they examined perished as a result of contact with surface oil.

Wilson⁽⁸⁵⁾ estimated that 5000 ducks were contaminated with oil in eastern Lake Ontario and the western portion of the St. Lawrence River in 1960. Foley⁽³⁰⁾ reported that 195 ducks banded in the Niagara River in the winter of 1960 carried oil. Furthermore, 11 that were clean when banded were later found dead and covered with oil. Records of the demise of more than 100 water birds in April 1961 were given by Collins. (24) A review of pollution problems in relation to wildlife losses, particularly waterfowl, in the Detroit River and Lake Erie was given by Miller. (63)

Lee⁽⁵⁵⁾ reported oil polution that caused the death of an estimated 500 waterfowl in 1951 on the upper Mississippi River. Peller⁽⁶⁶⁾ recorded a kill of at least 10,000 ducks in the Minnesota River in March, following the thawing of ice and release of accumulated crude and soybean oil. The crude oil had resulted from a broken pipe at an oil company and the soybean oil from a burst tank, both situated upstream.

Literature Cited Concerning Oil Pollution and Waterfowl

- 1. Adams, N. K. The Pollution of the Sea and Shore by Oil. Rept. to Council of the Royal Society, London. 27 pp. 1936.
- Aldrich, E. C. "A Recent Oil Pollution and Its Effect on the Water Birds in the San Francisco Bay Area," <u>Birdlore</u> 40(2), pp. 110-114. 1938.
- 3. Angus, K. C. (No Title). Address to International Conference on Oil Pollution of the Sea. Copenhagen, Denmark. 1959.
- 4. Anonymous. "The Attempted Rehabilitation of Oiled Sea Birds at Slimbridge, April-July 1967," Interim Report (unpub. mimeo), The Waterfowl Trust, Slimbridge, England. 9 pp. 1967.
- 5. Anonymous. "Oil Spillage Imperils More Ducks," New York Herald Tribune, N.Y. Jan. 12, 1961.
- 6. Anonymous. "Shorebirds Die in Hundreds as Oil Pollutes Beaches," Edgartown. Mass. Gazette. Dec. 30, 1960.
- 7. Anonymous. "Thousands of Ducks Die in Detroit River Oil Slick," Michigan Out-of-Doors. (April) 11(4). 1960.
- 8. Audubon Editor. "The Menace of Oil Pollution." Audubon Mag. vol. 59, pp. 24-25, 34-35, 81-82. 1957.
- 9. Barclay-Smith, P. "The British Contribution to Bird Protection," Ibis 101(1) pp. 115-129. 1959.
- Barclay-Smith, P. "Oil Pollution of the Sea. The Present Situation and Measures Taken to Prevent Oil Pollution," Rapp. Comm. Int. Explor. Sci. Mer. Medit., vol. 14, pp. 553-556. 1958.
- 11. Barclay-Smith, P. "Oil Pollution of the Sea," VII Bull, Int. Council for Bird Preservation, pp. 51-53, 1958.
- 12. Barclay-Smith, P. "Oil Pollution," <u>Bird Notes</u>, vol. 27, pp. 81-83. 1956.
- 13. Beatty, R. O. "Wildlife's Stake in Pollution Abatement," Trans. 13th N. Am. Wildlife Conf., pp. 563-595, 1948.

- 14. Bergström, J. "Olje Skandalerna Forsätter," Sveriges Natur, vol. 48, 1, pp. 8-10. 1957.
- Bourne, W. R. P., J. D. Parrack, and G. R. Potts. "Birds Killed in the TORREY CANYON Disaster," Nature, vol. 215, pp. 1123-1125. 1967.
- 16. Boyer, G. F. Oiling of Sea Birds and Other Waterfowl, Informal report to Chief, Canadian Wildlife Service, Ottawa, Canada, April 29, 1950.
- 17. Boyer, G. F. Oil Pollution. Informal report to Chief, Canadian Wildlife Service, Ottawa, Canada, April 29, 1948.
- 18. Brouwer, G. A. "Beiträge zur Frage der Ölpest," Die Vogelwarte, 16(4), pp. 167-170. 1953.
- 19. Brown, P. E. Destruction of Sca-Birds, Proc. Int'l. Conf. on Oil Pollution of the Sea, Copenhagen, Denmark, pp. 71-73, 1959.
- 20. Bruijns, M. F. M. "Birds as Victims of Oil Pollution on the Coast of the Netherland," Levende Nat., 62(8), pp. 172-178. 1959.
- 21. Bruijns, M. F. M. "The Numbers of Oiled Birds Found Dead on the Coast of the Netherland, 1948-58," Proc. Int'l Conf. on Oil Pollution of the Sea, Copenhagen, Denmark, pp. 75-76. 1959.
- 22. Burnett, F. L. and D. E. Snyder, "Blue Crab as Starvation Food of Oiled American Eiders," Auk. 71(3), pp. 315-316. 1954.
- 23. Callaghan, J. "International Aspects of Oil Pollution," Trans. 26th N. Amer. Wildlife Conf., pp. 328-342. 1961.
- 24. Collins, C. T. "Oil Pollution--Again!" Jack-Pine Warbler, 39(3), pp. 129-130, 1961.
- 25. Dennis, J. V. Oil Pollution Survey of the Great Lakes Within United States Territorial Limits. American Petroleum Institute, Wash. D. C. 22 pp. 1960.
- 26. Dennis, J. V. "Can Oil Pollution Be Defeated?" Mass. Audubon Mag., 44(2), pp. 66-73. 1959.
- 27. Dennis, J. V. "Losses to Birdlife," Oil Pollution Survey of the United States Atlantic Coast. Amer. Petrol. Inst., Div. Transportation, Wash. D. C., pp. F26-F28. 1959.
- 28. Erickson, R. C. "Effects of Oil Pollution and Migratory Birds,"
 Biological Problems in Water Pollution, 3rd seminar (1962). R. A.
 Taft San. Eng. Cent., Cincinnati, Ohio, pp. 177-181. 1965.

- 29. Erickson, R. C. "Oil Pollution and Migratory Birds," Atlantic Naturalist, 18(1), pp. 5-14. 1963.
- 30. Foley, D. Evaluation of Hunting and Other Decimating Factors. Waterfowl Mgmt. Res. Rept., Proj. W-39-R-13, Job IV-D. N. Y. Conserv. Dept., Div Fish and Game, Albany, N. Y. 1960.
- 31. Galtsoff, Paul S. "Oil Pollution in Coastal Waters," Proc. N. Amer. Wildlife Conf., 1936., pp. 550-555. 1936.
- 32. Giles, L. A., Jr., and J. Livingston. "Oil Pollution of the Sea," Trans. 25th N. Amer. Wildlife Conf., pp. 297-303. 1960.
- 33. Gonder, P. "Government Action," TORREY CANYON Birds, 1(10), pp. 201-212. 1967.
- 34. Grenquist, P. "On Oil Damage on Finland's Territorial Waters in 1948-1955," Suomen Riista, vol. 10, pp. 105-116. 1957.
- 35. Hadley, A. H. "A Sea-Bird Tragedy," <u>Bird Lore</u>, 32(2), pp. 169-172. 1930.
- 36. Harrison, J. "Oil Pollution Fiasco on the Medway Estuary," Birds, 1(7), pp. 134-136. 1967.
- 37. Hartung, R. and G. S. Hunt. "Toxicity of Some Oils to Waterfowl," J. Wildlife Mgt., 30(3), pp. 564-570. 1966.
- 38. Hartung, R. "Some Toxic Effects of Ingesting Polluting Oils on Waterfowl," 4th Ann. Meeting Soc. Toxicol., Williamsburg, Va. March 8-10. 1965.
- 39. Hartung, R. "Some Effects of Oil on Reproduction of Ducks," J. Wildlife Mgt., 29(4), pp. 872-874. 1965.
- 40. Hartung, R. Some Effects of Oil on Waterfowl. Ph.D. Thesis, Univ. Mich., Ann Arbor., 190 pp. 1964.
- 41. Hartung, R. "Ingestion of Oil by Waterfowl," Papers Mich. Acad. Sci., vol. 48, pp. 49-55. 1963.
- 42. Hautekiet, M. R. "Vijf jaar stookolieslachtoffers," <u>Die Wielewaal</u>, vol. 11, pp. 289-294, 1955.
- 43. Hawkes, A. L. "A Review of the Nature and Extent of Damage Caused by Oil Pollution at Sea," <u>Trans. 26th N. Amer. Wildlife Conf.</u>, pp. 342-355. 1961.

- 44. Henneberg, R. "Olpest-beobachtungen auf Wangeroog," Beitr. Naturk. Niedersachs, vol. 8, pp. 102-105. 1955.
- 45. Horwood, H. "Death Has a Rainbow Hew," Canadian Audubon, 21(3), pp. 69-73, 1959.
- 46. Houldson, F. "Oil and the California Murre," Audubon Mag., March-April, pp. 118-121, 1952.
- 47. Hunt, G. S. "The Direct Effects on Some Plants and Animals of Pollution in the Great Lakes," <u>Bioscience</u>, 15(3), pp. 181-186. 1965.
- 48. Hunt, G. S. "Waterfowl Losses on the Lower Detroit River Due to Oil Pollution," <u>Proc. 4th Great Lakes Res. Conf.</u>, Univ. Mich., Ann Arbor, pp. 10-26. 1961.
- 49. Hunt, G. S. Causes of Mortality Among Ducks Wintering on the Lower Detroit River. Ph. D. Thesis, Univ. Michigan. (L. C. Card No. Nic. 58-1418). Ann Arbor, Mich. 1957.
- 50. Hunt, G. S., and Cowan, A. B. "Causes of Deaths of Waterfowl on the Lower Detroit River Winter 1960," Trans. 28th N. Am. Wildlife Conf., vol. 28, pp. 150-163. 1963.
- 51. Hunt, G. S. and H. E. Ewing. "Industrial Pollution and Michigan Waterfowl," Trans. 18th N. Amer. Wildlife Conf., vol. 18, pp. 360-368. 1953.
- 52. International Joint Commission. Report of the International Joint Commission, United States and Canada, on Pollution of Boundary Waters. Washington, D. C., and Ottawa, Canada. 1951.
- 53. Küchler. "Kampf der Ölpest," Falke, vol. 3, pp. 193-200. 1956.
- 54. Lane, F. W., A. D. Bauer, H. F. Fisher, and P. N. Harding.

 Effect of Oil Pollution on Marine and Wildlife. Rept. U. S. Fish.

 Comm. for 1925, App. V; Bureau of Fish. Doc. No. 995, pp. 171-181.
 1926.
- 55. Lee, F. B. "Waterfowl Mortality Due to Oil Pollution in the Vicinity of Red Wing, Minnesota," Flicker, 24(3), pp. 116-188. 1952.
- 56. Lincoln, F. C. Treatment of Oil-Soaked Birds. Wildlife Leaflet No. 221, U. S. Fish and Wildlife Service, 2 pp. 1942.
- 57. Lincoln, F. C. "The Effect of Oil Pollution on Waterfowl," Proc. N. Amer. Wildlife Conf., 1936, pp. 555-564. 1936.
- 58. Lindsay. C. E. and H. C. Tegeiberg. Razor Clam Mortalities at Pacific and Conalis Beaches, March 1964. Unpublished report, State of Wasi gton, Department of Fish., Res. Div., 22 pp. 1964.

- 59. Livingston, J. A. "Toll of Seabirds by Oil Worst in History," Press Release, Audubon Society of Canada, Toronto, Feb. 19, 1980.
- 60. Livingston, J. A. "The Senseless Slaughter of Our Seabirds," Macleans, 71(16), Toronto, Canada. 1958.
- 61. Martini, E. "Olpest Beobachtungen auf der Nordseeinsel Spiekeroog. Ornithol," <u>Miltel.</u>, 5(3), pp. 44-48. 1953.
- 62. Merrin, P. and B. S. Jackson. "R. S. P. B. Action," <u>TORREY CANYON</u> <u>Birds</u>, 1(10), pp. 201-212, 1967.
- 63. Miller, H. J. Pollution Problems in Relation to Wildlife Losses, Particularly Waterfowl. Detroit River and Lake Erie, Garne Div. Rept. No. 2370. Mich. Dept. Cons. 9 pp. 1962.
- 64. Miller, H. J. and S. C. Whitlock. "Detroit River Waterfewl Mortality Winter 1948," Mich. Conserv., 17(4), pp. 11 and 15. 1948.
- 65. Moffit, J. and R. T. Orr. "Recent Disastrous Effects of Oil Pollution on Birds in the San Francisco Bay Region," Calif. Fish Game, vol. 24, pp. 239-244, 1938.
- 56. Peller, E. "Operation Duck Rescue (Minnesota)," Audubon, 65(6), pp. 364-367, 1963.
- 67. Peterson, R. T. "Birds and Floating Oil," <u>Audubon</u>, 44(4), pp. 217-225, 1942,
- 68. Ranwell, D. S. and D. Hewitt. "Oil Pollution in Poole Harbor and Its Effect on Birds," <u>Bird Notes</u>, 31(6), pp. 192-197. 1962.
- 69. Richardson, F. "Sea Birds Affected by Oil from the Freighter SEAGATE," Murrelet, 37(2), pp. 20-22. 1956.
- 70. Ridder, M. de "Victims Ailees Du Mazout," Les Natural, Belges, vol. 42, pp. 145-156. 1961.
- 71. Ringleben, H. "Die Ölpest, eine Gefahr für die Seevögel," Natur und Volk, vol. 71, pp. 461-465. 1941.
- 72. Ripley, D. "Oil On the Sea," Audubon, 44(2), pp. 86-90. 1942.
- 73. Rittinghaus, H. "On the Indirect Distribution of the Oil Pest in a Sea Bird Sanctuary," Ornithol. Mitteil, 8(3), pp. 43-46. 1956.
- 74. Rook, D. "To Clean or Kill?". TORREY CANYON Birds, 1(10), pp. 201-212. 1967.

- 75. Spencer, R. "The Effect on Birds," TORREY CANYON Birds, 1(10), pp. 201-212. 1967.
- 76. Tâning, A. V. "The Oil Death," Sverig. Natur., vol. 5. 1952.
- 77. Tanis, J. J. C. and M. F. M. Bruijns. "Investigations on Sea Birds Killed by Oil Pollution (1958-1962)." <u>Levende Nat.</u>, 65(6), pp. 133-140. 1962.
- 78. Ticehurst, N. F. "Oiled Birds Resorting to Fresh Water," Brit. Birds, vol. 31, pp. 354-355, 1938.
- 79. Tuck, L. M. Oil Pollution Report Newfoundland, 1960. Informal Report, 1960 (mimeo), 28 pp. 1960.
- 80. Tuck, L. M. The Murres--Their Distribution, Populations and Biology, Canadian Wildlife Series: 1. Dept. of N. Affairs and National Resources, Nat'l. Park Branch, Cana. Wildlife Serv., Ottawa, Canada, 260 pp. 1960.
- 81. Tuck, L. M. and J. Livingston. "Oil Pollution in Newfoundland," Proc. Int. Conf. on Oil Poll. of the Sea, Copenhagen, Denmark, pp. 73-79.
- 82. Tufts, R. W. Preliminary Report Covering Investigation of Damage to Seafowl by Crude Oil Along the Nova Scotia Coast. Report to: Chief, Canad. Wildlife Serv., Ottawa, Canada. March, 1942.
- 83. Tufts, R. W. Informal Report on Investigation of Damage Being Done to Waterfowl in Coastal Nova Scotia as a Result of Floating Crude Oil. Report to The Comptroller, National Parks Bureau, Dept, Mines and Resources, Ottawa, Canada. May, 1942.
- 84. Williams, J. K. "Detergent and Wildlife," In: TORREY CANYON Birds, 1(1°), pp. 201-212. 1967.
- 85. Wilson, J. E. Oil Contamination in Relation to Waterfowl Kill Records, 1960, Lake Ontario, St. Lawrence River. Unpubl. Rept., N.Y. Conserv. Dept., Div. Fish and Game, Albany, 3 pp. 1960.
- 86. Wragg, L. E. "Effect of DDT and Oil on Muskrats," Can. Field Nat. vol. 68, pp. 11-13. 1954.

Addenda

87. Barclay-Smith, P. "Oil Pollution an Historical Survey," J. Devon Trust Nature Conservation (Suppl.), July, 1967, pp. 3-7. 1967.

- 88. Spooner, M. F. "Biological Effects of the TORREY CANYON Disaster,"

 J. Devon Trust Nature Conservation (Suppl.), July, 1967, pp. 12-19,
 1967.
- 89. Manwell, C. and C. M. Baker. "Oil and Detergent Pollution Past, Present, Politics and Prospects," J. Devon Trust Nature Conservation (Suppl.) July, 1967, pp. 39-72. 1967.

6.3 OIL POLLUTION AND AQUATIC PLANTS

Introduction

Aquatic plants are photosynthetic organisms, i.e., those life forms which possess the green pigment chlorophyll (sometimes hidden by other pigments) enabling them to combine water and carbon dioxide in the presence of solar energy to form starch, or related substances, and to produce oxygen. Aquatic plants, therefore, encompass numerous types of algae and diatoms, as well as vascular plants. Photosynthesis is absent in all typical bacteria, actinomycetes, fungi, yeasts and protozoa, as well as the higher organisms.

Aquatic plants are vital for the existence and maintenance of many forms of freshwater and marine animals. In addition to the production of oxygen, aquatic plants provide essential food, shelter, and sites for reproduction of invertebrates and vertebrates. According to Nelson-Smith, $^{(40)}$ fresh oil has serious effects on both marine plants and animals at between 0.01 and 0.1% concentration and kills them at 0.5 to 5.0%.

Mode of Toxicity

Crude oil and most fuel oils exert a toxic effect because of two main groups of constituents: the volatile aromatics such as benzene and certain phenolic substances such as the naphthenic acids. The more dangerous of the aromatics quickly evaporate, while the naphthenic acids are readily water-soluble. Oil spread out on the surface of the sea normally becomes chemically harmless quite quickly. (40)

According to McKee, ⁽³⁷⁾ "By spraying pure hydrocarbons on plants, it has been found that aromatics are most toxic, naphthenes and olefins intermediate in toxicity, and straight paraffins the least toxic. The low-boiling aromatics are highly toxic and within each series, the smaller molecules are more toxic. When oxidized, the hydrocarbons may become much more deleterious; indeed, aliphatic acids dissolved in oil enhance the toxicity owing to the fact that they remain undissociated in oil solution."

Studies by van Overbeek and Blondeau⁽⁴⁷⁾ indicate that hydrocarbons are toxic to plants only when they penetrate inside the cell. These workers maintain that the toxic action of oils is a chemical effect of solubilization of the plasma membrane and other lipophases of the plant. Theoretically, as hydrocarbons solubilize into the plasma membrane, they push the molecules apart and increase its permeability. The pressure inside of the cells thus forces the cellular contents into the intercellular spaces and the cells then collapse.

According to McKee, ⁽³⁷⁾ van Overbeek adds that "The smaller the hydrocarbon molecule, the more of them will solubilize and the more damage they will do. In water (irrigation), however, these smaller molecules will have evaporated unless they are carried in emulsified form in the water."

Farrar⁽¹⁶⁾ observed that the viscosity of a petroleum oil determines to a limited extent its toxicity to terrestrial plants. The lighter oils, with a Saybolt viscosity of 50 sec or less, are less tox c than oils of heavier viscosity. Oils of greater than 100 sec viscosity tend to create undefined physiological disturbances within growing plants.

Minshall and Helson⁽³⁸⁾ reviewed the herbicidal action of oils, with reference to the literature on petroleum oils. Currier and Peoples⁽¹³⁾ studied the phytotoxicity of five hydrocarbons as vapors distilled with air and in aqueous solutions. They noted little difference in absolute toxicity and ascribed the detected differences to physical factors involving movement and retention of molecules at the site of physiological action. Ginsberg⁽²¹⁾ made an early study of the penetration of refined petroleum oils into the tissues of terrestrial plants. He noted high penetration of oils of low viscosity (leaf injury only followed penetration) and low penetration of emulsified oils. Young⁽⁵⁹⁾ has given an erudite discussion of the oil-mass theory of petroleum oil penetration into plant cytoplasm.

The herbicidal properties of petroleum hydrocarbons were reviewed by Havis, (22) using 31 pure compounds which were applied to terrestrial plants. Aromatics, naphthenes, olefins, and straight-chain paraffins were increasingly toxic, and the boiling point influenced toxicity independently of the hydrocarbon series. Nontoxic oils penetrated plant tissue, but not the living cells. Toxicity appeared to be associated with cell penetration.

McKee⁽³⁷⁾ briefly reviews investigations on the effects of application of crude oil to crops by contaminated irrigation waters. In general, oily wastes in irrigation waters did not appear harmful to plant life.

Review of the Literature

The widespread agricultural use of petroleum oils and various petroleum products to control weeds documents their phytotoxic action. When properly applied for the elimination of weedy grasses, oils do not harm crop plants by accumulation of toxic residues in the soil. Although toxic effects of crude oil and petroleum products may first be evident, like all organic compounds they are ultimately decomposed, largely by the action of microorganisms. The byproducts resulting from decomposition frequently benefit subsequent growths of vascular plants. In contrast to terrestrial plants, the interrelations of aquatic plants and oil are less well known.

Emergent Vegetation of Shorelines. Shaw and Timmons (52) demonstrated the effectiveness of light aromatic hydrocarbons in controlling submerged water weeds in irrigation ditches. The effective concentration of emulsified hydrocarbons was 300 ppm. Additional information on the control of rooted aquatic plants was provided by Bruns et al. (2) Hunt (25) stated that waste oils eliminated the emergent vegetation in a 500 to 1000 acre marsh along the southeastern shore of Lake Michigan, but that four years later the plant growth was again luxuriant. Currier and Peoples (13) found that some aromatic hydrocarbons rapidly killed various aquatic plants at the concentration of 1%.

Threshold concentrations for waste waters from tar distillation and phenol fractionation, in regard to toxicity for water plants, were found by Veldre⁽⁵⁷⁾ to be 1.0 and 0.05 ml/liter, respectively.

Mackin⁽²⁹⁾ studied the effects of crude oil upon salt-marsh plants which grow with their roots and part of their stems in tidal waters. He observed that saltgrass, saltwort, glasswort, cordgrass, young mangroves, and several other plants were harmed more readily by oil than were oysters. In one series of experiments, Mackin found that such plants were damaged

by 25 ml of crude oil per square foot of water surface. Previous studies (30, 31) revealed the rapid death of saltgrass and saltwort, but later the plants completely repopulated the area. Indeed, fertilization from the decomposition products resulted and a lush growth was produced. Mackin noted two stages in the disappearance of the oil: 1) rapid evaporation of lighter fractions from the surface and adherence of heavier fractions to the mud at low tide, and 2) slow decomposition of heavy fractions in the mud.

Diaz-Piferrer⁽¹⁴⁾ noted that crude oil from a wrecked tanker off
Puerto Rico settled around the roots of mangroves and, when deposits were
heavy, killed the plants. He stated that marine vegetation was seriously
affected, especially the plants living in intertidal and sublittoral zones.
Ranwell and Hewet⁽⁴⁸⁾ reported that an oil-contaminated <u>Spartina</u> marsh in
England was effected, but was restored by new growth the following season.

ZoBell⁽⁶⁰⁾ pointed out that it is common practice to kill grasses and algae growing in irrigation ditches with large slugs of oil emulsified in water, but that most submerged plants are killed only by relatively long exposure to rather high concentrations of soluble hydrocarbons.

Kelp. Clendenning⁽⁷⁾ studied the effects of diesel oil on the marine kelp, Macrocystic pyrifera. In control led laboratory experiments, a 0.02 m film had little effects on the bottom blades for 24 hr at 22 °C, but after three days exposure the photosynthetic activity was completely arrested. An emulsion of oil in sea water, consisting of oil globules 0.2 to 6µ diam, was more injurious. A 1.0% emulsion in sea water caused a 73% reduction in photosynthetic capacity in 24 hr; some inhibitory effect was noted by a 0.01% emulsion after three days exposure. The effects of the oil on the submerged blades was attributed partly to the action on the fatty constituents of the cytoplasmic membrane and partly to its content of toxic cresols and phenols.

Clendenning⁽⁶⁰⁾ also reported the effects of cresols and phenols on kelp. Heavy, black, highly aromatic fuel oils containing these substances were more toxic than light engine oils. The threshold of toxicity of phenol and o-cresol was only 0.1 ppm, but 10 to 100 times this concentration was needed to bring about complete inactivation of photosynthesis.

An anonymous account⁽¹⁾ reports that diesel and boiler fuel oil in concentrations of 1% by volume almost completely reduced photosynthetic activity of kelp (M. pyrifera) in 2 days, with boiler fuel being more toxic than diesel oil. Even a 3 hr exposure to 0.1% boiler fuel, followed by normal conditions, proved detrimental.

関係の表現のである。 1960年の 19

In March 1957, the oil tanker TAMPICO grounded off Baja California and spilled large quantities of diesel oil. A nearby kelp bed was exposed to the oil, which persisted for several weeks, but the kelp appeared to grow more profusely during the ensuing three months. North described the conditions and attributed the improved growth to the lethal action of oil on animals which feed on the kelp. North also studied the disappearance of kelp off sewer outfalls but concluded that toxic substances were not responsible. The disappearance of kelp was attributed to sea urchins, and the waste discharges appeared to provide favorable conditions for these animals.

Clendenning and North, (8) and North, Neushul and Clendenning (45) gave general discussions of the results of their earlier findings of the effects of emulsified fuel oil on M. pyrifera. North later gave a general account of the aftermath following the wreck of the tanker TAMPICO off Baja California in 1957. Seaweeds were not as seriously damaged as were animals by the released diesel oil; the greatest harm apparently resulted from pieces of wreckage scouring the rocks. The cove was rapidly repopulated with plants. Nelson-Smith observed increased growth of fucoid algae in Milford Haven, England, following long-term exposure to oil and attributed this to the destruction of invertebrates which normally grave on the plants.

Algae and Diatoms. Galtsoff et al. (16) found that a heavy layer of oil on the surface of culture flasks inhibited the growth of the marine diatom Nitzchia closterium. The authors concluded that crude oil discharged into the sea yields water-soluble substances that are toxic. The extract from the equivalent of 12% crude oil stimulated the growth of most Nitzchia cultures, the extract from 25% retarded growth, and the extract from 50% stopped growth. Studies by Chipman and Galtsoff demonstrated that the toxic

effects of fuel oil is often due to water-soluble substances in the oil, and that the toxicity of the oil is primarily a function of the concentration of the substances leaching into the water.

McKee, (37) in summarizing the effects of oil substances to aquatic life in freshwater, stated that: 1) free oil and emulsions may coat and destroy algae and other plankton, 2) heavy coatings of free oil on the surface may interfere with the natural processes of reaeration and photosynthesis, while light coatings would be less detrimental because wave action and other turbulence would maintain adequate reaeration, and 3) water soluble principles may exert a direct toxic action.

Studies by Gilet (20) in the harbor of Marseilles, a port characterized by floating patches of hydrocarbons, revealed 66 species of algae. The flora, however, developed best in the outer harbor where the water was more turbulent and less turbid. Mallet and Laimi (33) found that small amounts of 3, 4-benzopyrene type hydrocarbons or similar compounds accumulated in plankton of the LaRance estuary. George, (19) who examined marine organisms in Milford Haven after a series of accidents involving release of crude oil, stated that the marine algae, Pelvetia canaliculata and Fucus spiralis, appeared unaffected and continued to grow at a normal rate.

Diaz-Piferrer (14) found that oil pumped from the grounded tanker ARGEA PRIMA off Puerto Rico caused extensive damage to marine algae. Repopulation of algae in intertidal zones eventually followed, but in contrast to previous types, the forms were predominately blue-green algae.

According to Malina, (32) Korzep (28) evaluated the toxicity of various organic chemicals to the freshwater green algae, Chlorella pyrenoidosa, in laboratory studies. Among the petrochemicals, organic acids were least toxic followed by alcohols and amines, alkyl halides, aldehydes and ketones, with compounds of the benzene series exhibiting the highest toxicities. Malina also provided a breakdown of the various petrochemicals originating from crude petroleum and natural gas.

Reiman⁽⁴⁹⁾ noted that certain chemical components of oil, particularly the naphthenic acids, mercaptans, and phenol derivatives, are toxic to lower water organisms; unicellular algae may be damaged and

sink. Zobell⁽⁶⁰⁾ stated. "Despite the sensitivity of diatoms and other phytoplankton organisms to toxicity (of oil), laboratory as well as field observations suggest that such organisms seem to be injured only by continuous prolonged exposure to large amounts of oil. Such conditions prevail only in limited badly polluted areas such as tidepools, seaports, and settling ponds or lagoons." Føyn⁽¹⁷⁾ also concluded that, "Only a small effect of oil pollution on diatoms is found, and it can be stated that, in general, diatoms and other phytoplankton organisms seem to be injured only by continuous exposure to large amounts of oil."

McCauley, ⁽³⁶⁾ conducting an extensive study on the biological effects of oil pollution in a river, found that oil was markedly toxic to the plankton. However, several genera of freshwater algae were tolerant even when the oil pollution was at a maximum. Apparently the oil eliminated some plankton organisms sensitive to it, and the more tolerant organisms remained.

Water samples, according to Spooner, ⁽⁶¹⁾ were taken under the oil lost by the TORREY CANYON and samples of water and phytoplankton were obtained from areas of spraying and from where the oil had already been broken up by detergents. At first, the phytoplankton appeared quite normal. However, after being kept in the laboratory for about a week, some of the larger forms displayed abnormalities and most of the more delicate flagellates perished. When a third cruise was taken, the phytoplankton showed abnormalities and in some areas the plant crop was very poor. Observations indicated that the oil did little damage, but that the detergent probably had some effect on the plankton. Spooner ⁽⁶¹⁾ provided additional observations on the varying effects of oil and detergents on intertidal algae and lichens.

<u>Plants in Refinery Effluents.</u> Although plants occur in effluents from refineries, sometimes in abundance due to stimulation by essential nutrients, the variety of species is usually restricted. The composition of the flora is normally different than that existing in uncontaminated waters.

Crosby, Rudolfs, and Henkelekian⁽¹²⁾ reported the growth of blue-green algae (Oscillatoria) and bacterial zooglea was stimulated in waste waters from three petroleum refineries. Copeland and Dorris⁽¹¹⁾ studied

primary productivity arising from algal photosynthesis in two systems of oil refinery ponds. They observed that productivity and respiration decreased progressively during effluent travel through the systems. Copeland and Dorris (10) reported that algae in oil refinery effluents was less efficient in converting solar energy to chemical energy than algae in sewage communities or natural climax communities. Copeland, Minter, and Dorris (9) correlated concentrations of Chlorophyll A and suspended organic matter with photosynthetic production of oxygen in a series of refinery effluent holding ponds; phytoplankton appeared to be the major contributor of organic matter.

Minter, (39) who also enumerated biola in connected refinery effluent ponds, found that the standing crop of phytoplankton was greatest in ponds located midway in the series, and that species diversity increased as biomass decreased.

Effects of Detergents. There is circumstantial evidence that detergents, or emulsions of detergents, water, and oil, are considerably more toxic to plants than is oil alone. Although there are several types of emulsifying agents, soaps and synthetic detergents are commonly used for this purpose because they lower the surface tension. When surface tension is lowered, the interfacial area between the liquids can increase. Farrar, (16) working with petroleum-oil sprays on terrestrial plants, found that: 1) emulsions formed with soap are generally toxic to foliage irrespective of the saturation of viscosity of the oil, and 2) oil containing as much as 9% unsaturated hydrocarbons will cause injury in most cases if they are combined with soap emulsifiers. Only some of the pertinent references are noted below.

Freshwater Plants. Synthetic detergents were found to harm freshwater plants at concentrations of from 10 to 20 ppm by Roberts. (50)

Downing and Truesdale (15) gave preliminary results of the effect of soluble surface active agents on the rate of solution of oxygen in water. They observed that small concentrations caused considerable reduction of solution rates in distilled, tap, and saline water. These rates increased with increasing concentrations but tended to a limiting value. Klein (27) reported that freshwater plants of the common genera Potamogeton and

Ranunculus were liable to grow in waters containing 2.5 ppm or more of alkyl benzene sulfonate. Higher values were listed by Stedronsky and Truelle, ⁽⁵⁴⁾ who found synthetic detergents in laundry wastes were harmful to Elodea and Valligneria at concentrations of 50 ppm.

Heinz and Fischer (23) present a comprehensive review and list 176 references on detergents in water supplies. The review discusses biological and toxicological properties of detergents. Observations by Hynes and Roberts (26) in the River Lee, England revealed no changes in the fauna that could be correlated with detergent concentration; yet experiments showed that the scarcity of certain plant species could be due to detergents in the water. Cabejszek et al. (3) found that algae were killed by Sulfapol-50 (containing 50% sodium dodecyl benzene sulphonate) at concentrations exceeding 10 mg/liter, but that development of algal spores was stimulated.

Cairns. Scheier, and Hess, ⁽⁴⁾ evaluating effects of aklyl henzene sulfonate, found that the diatom <u>Nitzschia linearis</u> was not affected at concentrations below 5.8 mg/liter, and the 5 day TL_m was 10 mg/liter. In comparison, <u>Navicula seminulum</u> showed no growth reductions below 18 mg/liter and the 5 day TL_m was 39.4 mg/liter. The growth of diatoms was thus affected only by detergent concentrations higher than typical in surface waters of the U.S. Hicks and Neuhold ⁽²⁴⁾ utilized ¹⁴C to measure the effects of alkyl benzene sulfonate on communities of <u>Vaucheria</u> and <u>Cladophora</u>. ABS was found to have a negative effect on ¹⁴C uptake in both communities. However capacity for uptake partially recovered and was stimulated by exposure to low concentrations.

Additional information on the toxicity limits of detergents to algae in freshwater is provided by Sindelar and Marvan⁽⁵³⁾ and Matulova. ⁽³⁵⁾ Maloney⁽³⁴⁾ found that <u>Chlorella</u> prospered at concentrations of alkyl benzene sulphonate at 3.6 mg/liter, but greater concentrations resulted in inhibition of growth, with no growth occurring at 30 mg/liter.

Marine Plants. There is limited information on the effects of detergents on marine plants. Ukeles (55, 56) studied the effects of synthetic surface active agents on 12 species of marine phytoplankton. Growth

inhibition was more pronounced by nonionic surfactants as surface active properties increased. The tolerance of species belonging to the same family were similar, and each family displayed a specific inhibition pattern. All species were more sensitive to the cationic agents than to anionic agents. Clendenning and North stated that the cationic detergent Zephiran Chloride, a quaternary ammonium compound, was very poisonous to kelp, Macrocystic pyrifera, but the anionic detergent sodium dodecyl sulphate was not very toxic.

Detergents have been widely applied in recent years to rehabitate coastal areas contaminated by oil spills, but little factual data is available on the combined effects of detergents and oil emulsions on intertidal plants. George pointed out that the use of emulsifiers was followed by a severe mortality of intertidal organisms. His unpublished observations on the emulsifier used to clean up after releases of crude oil in Milford Haven, England demonstrated extreme toxicity to most flora living in the intertidal zone.

Detergents were widely applied in Britain to remove oil on both thick slicks at sea and accumulated deposits along the shore after the wreck of the TORREY CANYON. After briefly describing the effects of oil in comparison to detergents and oil, Williams concluded, "... the oil itself has done far less damage to life than the detergent which has been used." A similar conclusion was reached by O'Sullivan and Richardson and Nelson-Smith. Spooner concluded that the oil had little effect while at sea but that the detergent probably had some effect on the plankton.

Searle⁽⁵¹⁾ maintained that the oil from the TORREY CANYON and detergents were so diluted by sea water that the undersurface forests of kelp remained unharmed. However, in a cove near Porth Mear where 2000 gal of detergent were used to clean rocks of oil, limpets which graze on seaweeds were killed; as a result there was an uncontrolled spread of seaweeds. Williams⁽⁶²⁾ observed that where operations after the TORREY CANYON were conducted with care and on incoming tides, some of the fucoid seaweeds appeared healthy on rocks where the detergent did not reach. In other instances, however, the enormous amount of detergent applied left a smelly, lifeless area with remains of whitened seaweed in the pools.

According to Neison-Smith, (41) George added the equilifier that was used to clean shores of oil at Milford Haven to rock pools. Delicate algae were affected at 0.2% concentration and at 1% all but the coralline sca-weeds, which eventually repopulated the sea, were killed. Nelson-Smith⁽⁴¹⁾ also reviewed the effects of emulsifiers used to combat oil spills in Milford Haven and from the TORREY CANYON on various marine plants. In general, algae that were affected recovered and grew in greater abundance than previously. This appeared partially due to destruction of limpet snails. Nelson-Smith⁽⁴¹⁾ concluded that large brown algae survived oil-emulsifiers well, the delicate red algae were more severely affected, and the filamentous or sheet-like forms were also damaged.

It may be significant that marine seaweeds rapidly repopulated the cove effected by the wreck of the oil tanker TAMPICO off Baja California, according to North. (43) No detergents were amplied following this spill due to the isolation of the cove.

Literature Cited Concerning Oil Pollution and Aquatic Plants

- 1. Anonymous. "The Effects of Waste Discharges on Kelp," <u>Summary of Marine Waste Disposal Research Program in California</u>, State of Calif., Water Poll. Cont. Bd., Publ. No. 22, pp. 44-49. 1960.
- 2. Bruns, V. F., J. M. Hodgson, H. F. Arle, and F. L. Timmons. The Use of Aromatic Solvents for Control of Submerged Aquatic Weeds in Irrigation Channels. U. S. Dept. Agric., Circular No. 971, 1955.
- 3. Cabejszek, I., J. Just, J. Luczak, and J. Maleszeuska. "Influence of Sulfapol-50 on Physico-chemical Properties and Biocenosis of Water," Gaz Woda Tech. Sanit., vol. 37, pp. 53-57. 1963.
- 4. Cairnes, J. Jr., A. Scheier and N. E. Hess. The Effects of Alkyl Benzene Sulfonate on Aquatic Organisms. Ind. Water and Wastes, vol. 9, pp. 22-28. 1964.
- 5. Chipman, W. A. and P. S. Galtsoff. Effects of Oil Mixed with Carbonized Sand on Aquatic Animals. Spec. Sci. Rept. Fisheries, USFVS, vol. 1, pp. 1-52. 1949.
- 6. Clendenning, K. A. The Effects of Waste Discharges on Kelp: Phenols and Cresols. Univ. Calif. Inst. Mar. Resources, Ref. 60-4, pp. 45-47. 1960.
- 7. Clendenning, K. A. The Effects of Waste Discharges on Kelp: Fuel Oil. Univ. Calif. Inst. Mar. Resources, Ref. 59-4. pp. 4-12. 1958.
- 8. Clendenning, K. A. and W. J. North. "Effects of Wastes on the Giant Kelp, Macrocystic pyrifera," Waste Disposal in the Marine Environment (E. A. Pearson, Ed.). Proc. 1st International Conf., Pergamon Press, N. Y., pp. 82-91. 1960.
- 9. Copeland, B. J., K. W. Minter, and T. C. Dorris. "Chlorophyll and Suspended Organic Matter in Oil Refinery Effluent Holding Ponds. Limnol. Oceanog., 9(4), pp. 500-506. 1964.
- 10. Copeland, B. J. and T. C. Dorris. "Community Metabolism in Ecosystems Receiving Oil Refinery Effluents," <u>Limnol. & Oceanog.</u>, 9(3), pp. 431-447.
- 11. Copeland, B. J. and T. C. Dorris. "Photosynthetic Productivity in Oil Refinery Effluent Holding Ponds," J. Water Cont. Fed. 34(11), pp. 1104-1111. 1962.
- 12. Crosby, E. S., W. Rudolfs, and H. Heukelekian. "Biological Growths in Petroleum Refinery Waste Waters," Ind. Eng. Chem., 46(2), pp. 296-300. 1954.

- 13. Currier, H. B., and S. A. Peeples. "Phytotoxicity of Hydrocarbons," Hilgardia, 23(6), pp. 155-173. 1954.
- 14. Diaz-Piferrer, Manuel, "The Effects of an Oil on the Shore of Guanica, Puerto Rico," <u>Deep Sea Research</u>, 11(5), pp. 855-856. 1962.
- Downing, A. L. and A. G. Truesdale. "Some Factors Affecting the Rate of Solution of Oxygen in Water," J. Appl. Chem., London vol. 5, pp. 570-581. 1955.
- 16. Farrar, M. D. "The Effect of Petroleum-oil Sprays on Insects and Plants," Bull. Ill. Nat. Hist. Survey, 21(1), pp. 1-32. 1936.
- 17. Foyn, E. "Disposal of Waste in the Marine Environment and the Pollution of the Sea," Oceanogr. Mar. Biol. Ann Rev., vol. 3, pp. 95-114, 1965.
- 18. Galtsoff, P. S., H. F. Prytherch, R. O. Smith, and V. Koehring.

 Effects of Crude Oil Pollution on Oysters in Louisiana Waters. U. S.

 Bur. Fish, Bull. No. 18, pp. 143-210. 1936.
- 19. George, M. "Oil Pollution of Marine Organisms," <u>Nature</u> 192, (4808), p. 1209, 1961.
- 20. Gilet, R. "Water Pollution in Marseilles, and its Relation with Flora and Fauna," Proc. 1st Int. Conf., Waste Disposal in the Marine Environment. Pergamon Press, London, pp. 29-56, 1960.
- 21. Ginsberg, J. M. "Penetration of Petroleum Oils into Plant Tissue," J. Agri. Res., vol. 43, pp. 459-474. 1931.
- 22. Havis, J. R. "Herbicidal Properties of Petroleum Hydrocarbons,"

 Cornell Agri. Expt. Sta. Mem. 298. 1950. Chem. Abst., vol. 45,
 p. 21321. 1951.
- 23. Heinz, H. J. and W. K. Fischer. "Detergents in Water and Sewage," Fette Seif. Anstrichn., vol. 64, p. 270. 1961. Public Health Eng. Abst., vol. 43, p. 1531. 1963.
- 24. Hicks, C. E. and J. M. Neuhold. "Alkyl Benzene Sulfonate Effects on Stream Algae Communities," <u>Bull. Environmental Contam.</u> and <u>Toxicol.</u>, vol. 1, p. 225. 1966.
- 25. Hunt, G. S. "The Direct Effects on Some Plants and Animals of Pollution in the Great Lakes," <u>Bioscience</u>, 15(3), pp. 181-186. 1965.

- 26. Hynes, H. B. N., and F. W. Roberts. "The Biological Effects of Synthetic Detergents in the River Lee, Hertfordshire," Ann Appl. Biol. 50(4), pp. 779-790. 1962.
- 27. Klein, L. Aspects of River Pollution. Academic Press, Inc., New York, p. 621, 1957.
- 28. Korzep, D. A. <u>Toxicity of Organic Compounds</u>. Thesis, Univ. of Texas, Austin, 1962.
- 29. Mackin, J. G. Effects of Crude Oil and Bleedwater on Oyster and Aquatic Plants. Texas A. & M. Res. Found., Project 9 Rep. (mineo), p. 54, 1950a.
- 30. Mackin, J. G. A Comparison of the Effects of Application of Crude Petroleum to Marsh Plants and to Oysters, Texas A. & M. Res. Found., Project 9 Rep. (mimeo), p. 4. 1950b.
- Mackin, J. G. Report on a Study of the Effect of Application of Crude Petroleum on Saltgrass, Distichlis spicata (L.) Greene, Texas A. & M. Res. Found., Project 9 Rep. (mimeo), p. 8. 1950c.
- 32. Malina, J. F. "Toxicity of Petrochemicals in the Aquatic Environment," Water and Sewage Works, 111(10), pp. 456-460. 1964.
- 33. Mallet, L. and R. Lami. "Pollution of the Plankton by 3, 4-benzopyrene Type Polybenzene Hydrocarbons in La Rance Estuary," C. R. Soc. Biol., 158(12), pp. 2261-2262, 1964.
- 34. Maloney, T. E. "Detergent Phosphorus Effect on Algae," J. Water Poll. Cont. Fed., 38(1), pp. 38-45. 1966.
- 35. Matulova, D. "The Effects of Detergents on Water Algae," Vodni Hospodarstvi (in Czech.), 14(10), pp. 377-378. 1964. Chem. Abs., vol. 62, p. 10210h. 1965.
- 36. McCauley, R. N. "The Biological Effects of Oil Pollution in a River," Limmol. Oceanog. 11(4), pp. 475-486. 1966.
- 37. McKee, J. E. Oily Substances and Their Effects on the Beneficial
 Uses of Water. Publ. No. 16, State Water Poll. Cont. Bd., Sacramento,
 Calif., p. 72. 1956.
- 38. Minshall, W. H. and V. A. Helson. "The Herbicidal Action of Oils," Proc. Amer. Hort. Soc., vol. 53, pp. 294-298, 1949.

- 39. Minter, K. W. Standing Crop and Community Structure of Plankton in Oil Refinery Effluent Holding Ponds. Ph. D. Thesis, Okla, State Univ., p. 104. 1964.
- 40. Nelson-Smith, A. "Oil, Emulsifiers, and Marine Life," Conservation and the TORREY CANYON, J. Devon Trust for Nature Conservation (Suppl.), pp. 29-33. 1967a.
- 41. Nelson-Smith, A. "The Effects of Oil Pollution and Emulsifier Cleansing on Shore Life in South-West Britain," J. Appl. Ecol. 4(in press). 1967b.
- 42. North, W. J. "TAMPICO, a Study of Destruction and Restoration," Sea Frontiers, vol. 13, pp. 212-217. 1967.
- 43. North, W. J. An Investigation of the Effects of Discharged Wastes on Kelp. Calif. State Water Qual. Cont. Bd., Publ. No. 26, p. 176, 1964.
- 44. North, W. J. Successive Biological Changes Observed in a Marine Cove Exposed to Large Oil Spillage. Univ. Calif., Inst. Mar. Res., Ref. 62-6, pp. 1-33. 1961.
- North, W. J., Neushul, Jr., and K. A. Clendenning. "Successive Biological Changes Observed in a Marine Cove Exposed to a Large Spillage of Mineral Oil," Pollutions Marines par les Microorganismes et les Produits Petroliers. Comm. Intl. Pour L'Exploration Scientifique de la mer Méditeranée, Symposium de Monaco, April, 1964, pp. 335-354. 1965.
- 46. O'Sullivan, A. J. and A. L. Richardson. "The TORREY CANYON Disaster and Intertidal Marine Life," Nature, vol. 214, pp. 448, 541-542.

4 :

- 47. Overbeek, J. van and R. Blondeau. "Mode of Action of Phytotoxic Oils," Weeds, vol. 3, pp. 55-65. 1954.
- 48. Ranwell, D. S. and D. Hewett. "Oil Pollution in Poole Harbor and its Effect on Birds," <u>Bird Notes</u> 31(6), pp. 192-197. 1962.
- 49. Reimann, K. "Harmfulness of Oil and Tar Products to Lower Water Organisms," <u>Much. Beitr, Abwass, Fisch.</u> u FlussBiol., vol. 9, pp. 60-72. 1962.
- 50. Roberts, F. W. "Some Residual Effluent Problems," Water-Sanit. Eng., vol. 5, pp. 13-15. 1954.
- 51. Searl, D. "First Report on TORREY CANYON Coast, Ecology," The Sunday Times, London, Sept. 3, 1967.

- 52. Shaw, J. M. and F. L. Timmons. <u>Controlling Submersed Water Weeds in Irrigation Systems with Aromatic Solvents</u>. U. S. Bur. Reclam., U. S. Dept. Agriculture, 1949.
- 53. Sindelar, VI. and P. Marvan. "Toxicity of Flotation Reagents for Aquatic Organisms," Bergakademie 17(2), pp. 103-107. 1965.
- 54. Stedronsky, E. and M. A. Truelle. "Harmful Effects of Detergents on Aquatic Plants," Cölke Ryb, vol. 13, p. 70. 1958. Sci. Paper. Inst. Chem. Technol., Prague, Technol. Wat. 5(1), p. 563. 1961. Water Poll. Abst. (Brit.) vol. 37, p. 1521. 1964.
- 55. Ukeles, R. "Inhibition of Unicellular Algae by Synthetic Surface Active Detergents," J. Phycol. 1(3), pp. 102-110. 1985.
- 56. Ukeles, R. "The Effect of Surface Active Agents on the Growth of Marine Phytoplankton," 16th Meeting of the Soc. Protozool. J. Protozool. 10 (Suppl.), p. 10(abstract only). 1963.
- 57. Veldre, I. "Toxilogical Characteristics of Shale Waste Waters," Rybn Khoz. Vnute. Vodoemov Latv. SSR Sb., pp. 55-59. 1963. Chem. Abst., vol. 61, p. 14345. 1966.
- 58. Williams, J. K. "Detergent and Wildlife," <u>TORREY CANYON</u>, p. 207-208. <u>Birds</u> 1(10), pp. 201-212. 1967.
- 59. Young, P. A. "Oil-mass Theory of Petroleum-oil Penetration into Protoplasm," Amer. J. Bot., vol. 22, pp. 1-8, 1935.
- 60. ZoBell, C. "The Occurrence, Effects, and Fate of Oil Polluting the Sea," Int'l. Conf. on Water Pollution Res., London, 3-7 Sept.; Sect. III, p. 27, 1962.

Addenda

- 61. Spooner, M. F. <u>Biological Effects of the TORREY CANYON Disaster</u>, J. Devon Trust Nature Conservation (Suppl.), July, 1967, pp. 12-19. 1967.
- 62. Williams, J. K. The Extent of Pollution, J. Devon Trust Nature Conservation (Suppl.), July, 1967, pp. 20-22. 1967.

6.4 OIL POLLUTION AND OTHER LIFE FORMS

Numerous organisms (invertebrates) other than economically important forms such as molluscs inhabit aquatic environments. Species that dwell in freshwater are generally distinct from marine forms, although representatives of many taxonomic groups may occur in both habitats. Although the economic benefits of the "minor" invertebrates are not readily evident, these organisms are important in nutrient cycles and food chains that lead to the production of flora and fauna utilized by man. An important characteristic of these forms is a high reproductive capacity, which permits repopulation of depleted areas. Repopulation usually follows quite rapidly once the source of contamination is eliminated and the toxic compounds disperse or decompose. At the present time, only fragments of information concerning the effects of oil pollution and detergents on many of these organisms are available.

Manwell and Baker (72) provide an erudite discussion of oil and hydrocarbon-oxidizing bacteria which generally reproduce rapidly. In the summarized conclusions were the following pertinent statements:

- 1) A single oil spill kills many animals, depending on the variable toxicity of oil products and the size of the spill.
- 2) Chronic oil pollution leads to oxygen depletion and a consequent reduction in the number of species.
- 3) Oil is removed naturally at a slow but significant rate.
- 4) The present "oil spill" detergents are very toxic to many aquatic animals and, furthermore, are not readily degraded, leading to the possibility of food chain accumulation.

Microscopic Organisms

Bacteria. According to ZoBell, ⁽⁶⁷⁾ "There is no evidence that any bacterial species occurring in sea water or marine sediments are injured directly by oil pollution. Certain species may be able to compete with hydrocarbon-oxidizing bacteria which generally reproduce rapidly in the presence of oil in marine environments. Whereas the bacterial population of pure sea water normally ranges from ten or less to a few thousand per milliliter, it is not uncommon to find millions of bacteria per milliliter of

oil-polluted sea water or bottom sludge." He added, "With few exceptions, hydrocarbons and their derivatives are neither bacteriostatic nor bactericidal in ordinary concentrations." In fact, "The growth of oil-oxidizing bacteria is believed to be beneficial to the food chain in the sea, because such bacteria are eaten by numerous animal (protozoan) species." Rodina (54) reviewed some of the extensive literature on the contribution of bacteria to the nutrition of aquatic animals. Voroshilova and Dianova stated that the water becomes progressively enriched with bacteria and next with protozoa; the protozoa in turn are devoured by higher animals.

ZoBell⁽⁶⁷⁾ reported that oil-oxidizing bacteria convert an average of 30 to 40% of the carbon content of hydrocarbons into bacterial cell substance or protoplasm. Thus, for each gram of oil oxidized, 300 to 400 mg of animal food might be manufactured by bacteria. Malina⁽²⁹⁾ pointed out that almost every organic compound will be decomposed microbially, provided the required nutrients are available and sufficient time is allowed for the bacteria to adapt to the substrate.

That some oily wastes may serve as nutrient material and thus stimulate the growth of microorganisms was demonstrated by Crosby, Rudolfs, and Heukelekian (10) in their study of biological growths in petroleum refinery waste waters, and by Minter (37) in his study of plankton-in-oil-refinery effluent holding ponds. Mackin (26) found that bacteria and protozoa developed in abundance in experimental compartments used to study the effects of crude oil on saltgrass.

Emulsifiers in water have varied effects on bacterial growth. Manganelli and Crosby (30) showed that slime growths and autochthonous microorganisms in sewage were influenced by synthetic detergents. Low concentrations of anionic and nonionic detergents stimulated the growth of slime, while cationic detergents retarded it. Anionic and cationic detergents decreased oxidizing, purifying, and nitrifying capacities of bacteria in activated sludge, but nonionics produced no detrimental effects.

Lambin, Carrere and DeValamont (24) isolated the bacterium Pseudomonas and various enterobacteria from sewage that were resistant to sodium lauryl sulphate.

According to Spooner, ⁽⁶⁹⁾ oil-decomposing bacteria are fairly resistent to detergents and have not generally been poisoned by the residual concentrations that they have encountered. She implied that the dispersal of oil by detergents is beneficial to bacteria since they require an abundant supply of oxygen and are not able to act effectively on thick masses of oil.

Protozoa. Decomposition of oil by bacteria tends to increase the abundance of associated protozoa, provided that no toxic substances occur in the water. Yet, few quantitative determinations of this phenomenon have been made. In addition to Mackin's (26) observations, Belikhova (3) found that protozoa were among the organisms that survived treatment of river water with petroleum. McCauley (35) found the protozoans Euglena. Trachelomonas, and Vorticella among the plankters that tolerated the highest concentrations of oil in a river. Both Belinkova and McCauley believed that toxic substances in the oil eliminated some plankton organisms sensitive to them, while the more tolerant organisms remained.

Detergents may prove harmful to protozoa and inhibit their development in oil-contaminated waters. Manganelli and Crosby (30) found that anionic and cationic detergents had a marked detrimental effect on stalked and free-swimming protozoa in activated sludge.

Macroscopic Organisms

Mode of Toxicity. Available evidence indicates that the danger to macroscopic organisms from oily wastes is primarily from toxic watersoluble substances. However, free oil and emulsions may coat the respiratory surfaces and interfere with resolution, and in some cases the decomposition of oil may deoxygenate the water sufficiently to kill. McKee (36) noted that the toxicity of soluble substances arising from petroleum may be acute or cronic in action. He stated that acute toxicity produces death or debility in 96 hr or less. Chronic toxicity exerts a long-term effect, is difficult to detect, and is even more difficult to prove.

Malina (29) remarked that most bloassays evaluate the acute toxicity of a substance, and only some data estimate the chronic or cumulative effects of various toxicants over relatively long periods of time. He added,

"The synergism, antagonism, and other interactions of a multicomponent chemical system have not been accurately estimated." Also, "It is important to note that the same compound exhibits varying degrees of toxicity for different species of the test animals." Consequently, caution is necessary for observing, testing, and evaluating the effects of petroleum, petroleum products, and detergents on aquatic macroinvertebrates. One must assume some effects which may be either harmful or beneficial, since these compounds are not normal constituents of the aquatic environment.

Floating oil apparently has little influence on the gaseous exchange between water and the atmosphere. Weibe (65) claimed that oxygen adsorption in unaerated freshwater aquaria was inhibited by even a thin layer of oil. However, experiments by Brown and Reid (5) and Boswell (4) showed that a layer of crude oil on seawater caused only a slight reduction in the amount of oxygen absorbed from the atmosphere. According to Nelson-Smith, (39) films of oil more than a half-inch thick have very little effect on the aeration of even stagnant tidepools. McCauley (35) concluded that thin surface films of bunker oil on the surface of a river excluded some oxygen, but not enough to destroy planktonic organisms. Under natural conditions, with wind and wave action as well as currents, reduction of oxygen diffusion through oil films is not usually sufficient to harm most aquatic organisms.

Detergents have some effect on oxygen levels of water. Downing and Truesdale 14 found that small amounts of surface-active agents, under certain conditions of surface agitation, caused considerable reduction in rates of oxygen solution in distilled, tap, and saline water. Chambon (7) reported that dissolved oxygen in polluted river water may be increased by the action of detergents in liberating oxygen absorbed on suspended particles, and at the same time, retard oxidation of substrates. Alkyl benzene sulphonates retarded oxidation to a greater extent than alkyl sulphates

Review of Literature. Studies on the effects of oil pollution on macroinvertebrates generally evaluate acute toxicity, that is, toxicity producing death or obvious damage soon after exposure. Since the composition of macrofauna is widely diverse and varies in different areas,

and even with the season, relatively few species have been investigated. In the sea, the most harmful effects of oil occur in inshore waters where the greatest numbers and species of macroinvertebrates dwell, and then primarily in areas between high and low tide levels.

Of the animals tested by Chipman and Galtsoff (8) in their studies using oil mixed with carbonized sand, the hydrozoan <u>Turbularia crocea</u> was the most sensitive. It was killed quickly in water containing relatively small amounts of extracts from certain oils, but survived other oils. The toxicity of the injurious oils was due to substances that leached into the water. Toxicity to sedentary animals was evident whether the oils were on the surface of the water or were adsorbed by sand and held on the bottom.

Reish and Winter (52) found lumps of asphalt on the bottom and a strong sulfide odor in some areas near oil well operations in Los Alamitos Bay, California. However, the bottom supported a rich and varied fauna consisting of 70 species. In the Port of Marseilles, France, which is grossly polluted with floating hydrocarbons, Gilet (17) found that:

1) the quality of the Port water created no barrier for planktonic animals, and the larvae of open sea organisms entered without difficulty,

2) fauna did not occur at the surface where hydrocarbons were deposited, but were common below, and 3) the fauna of the surface layer disappeared under the influence of hydrocarbons. Clendenning and North (9) reported that emulsions of diesel oil in sea water caused the death of sea urchins.

North discussed mortalities of intertidal organisms exposed to diesel oil after the wreck of the TAMPICO in 1957 off Baja California. The macroinvertebrates most seriously affected, exclusive of molluscs and crustacea, included sea urchins, barnacles, and sea stars; intertidal anemone survived this severe pollution. Later reports by North and North, Neushul, and Clendenning claimed that abundant growth of giant kelp occurred after this accident because of mortalities of grazing animals, primarily sea urchins. Apparently only two animals, a small molluse and green anemone, survived the initial spill. A redescription of the aftermath of the TAMPICO spill was given by North.

According to Diaz-Piferrer, (12) crude oil from the wreck of the ARGEA PRIMA off the coast of Puerto Rico caused a severe mortality rate of marine organisms. Adult and juvenile lobsters, crabs, sea urchins, sea cucumbers, gastropods, octopuses, squids, a variety of fishes, and even sea turtles were found dead.

George (16) summarized observations on marine life following releases of crude oil in Milford Haven, England. Oil was deposited in bands along the shore in accordance with successive tides, the lighter fractions evaporated and a tarry residue that was resistant to leaching by moderate wave action was left. The oil, which was ingested by limpets and covered acorn barnacles, appeared to be nontoxic. Destruction of marine macroinvertebrates associated with several oil spills in Milford Haven, England was attributed by Nelson-Smith (39) to result not from the oil, but primarily from detergents used in removal. Mackin and Sparks (27) listed macroscopic marine invertebrates from areas exposed to various concentrations of oil from a wild-well off Louisiana. The oil appeared to exert little effect on the faunal communities that were normally present.

Reish⁽⁵¹⁾ studied the species of benthic animals in Los Angeles Harbor, California exposed to wastes from an oil refinery. A direct relation existed between high waste water volume (10 mgd), high organic carbon low dissolved oxygen, and a reduced number of species.

Apparently, the high oxygen demand of the decomposing wastes destroyed much of the ambient fauna. Studies by Tubb and Dorris ⁽⁶¹⁾ revealed that population fluctuations of midge fly larvae in oil refinery effluent ponds was related to toxicity of the wastes.

The biological effects and complex interrelations of oil pollution in a river was studied by McCauley. (53) The initial oil film on the water diminished with time, but sedimentation of the oil deposited oily sludge on the river bed. In the sediments the amphipod Gammarus Agrion nymphs, and the planarian Dugesia were unable to tolerate sludge conditions, while Tubifex and Tendipes as well as Nemata and Hirudinea types were tolerant and remained among the plankters. The rotifers Asplanchna, Keratella, and Polyartha, the crustacean Cy lops, and Nemata types

tolerated the highest concentrations of oil sludge. Slow decomposition of sludge resulted in low biocnemical oxygen demands.

Several papers which concern loss of i in macroinvertebrates resulted from the recent TORREY CANYON a ter. O'Sullivan and Richardson (46,71) list and discuss the organisms and dead at two sites, but mortalities presumably resulted from a combination of the spill of crude oil and subsequent application of detergents. Listed were sea anemones, polychaete annelids, barnacles, isopods, amphipods, decapods, and molluses. According to Williams, (66) observations of the Cornwall Naturalist Trust showed that littoral life, even on grossly polluted beaches, had been surprisingly unaffected by the initial spill of a. Some anemones had been killed, but most molluses remained healthy. He believed that the oil released by the TORREY CANYON would have done far less damage to life than the detergent which was used later. Glude and Peters a and Spooner a reached similar conclusions.

Nelson-Smith⁽³⁹⁾ believed that crude oil from the TORREY CANYON lost most of its toxic constituents while still afloat. He stated that, while many plants and animals might have been killed either by residual toxic substances or by the blanketing effect of a thick oil film, there were usually some survivors in protected situations nearby. At less heavily polluted shores, limpets, other gastropods, mussels, and anemones appeared healthy even though smeared with oil. Copland ⁽⁶³⁾ gives a map illustrating the degree of oil pollution along the Cornish coast following the TORREY CANYON episode.

The aftermath of the wreck of the tanker TAMPICO off Baja California in 1957, as reviewed by North (41), was uncomplicated by subsequent use of detergents. About 60,000 gal. of diesel oil were lost, and a completely natural cove was destroyed on a large scale. Among the dead species found were lobsters, abalone, sea urchins, starfish, mussels, clams, and a host of smaller forms. Only a few animals species survived, including green sea anemonies and a small snail, <u>Littorina</u>. The unsightly and poisonous condition lasted about three months, but repopulation of minor invertebrates soon took place.

Belikhov⁽³⁾ examined a section of the Volga River, USSR after spills of petroleum products. Some plankton and some bottom forms had high survival rates, although the oil reduced the growth of organism complexes for over a year. Belikhov suggested that the restricted toxic effects were due to the low solubility of poisonous petroleum products, and that some hydrobionts gave rise to generations that were more resistant to oil pollution.

Reimann (50) and Klinke (23) discussed the detrimental effects of oil and tar products to freshwater organisms. Malacea et al. (28) reviewed the effects of oil, naphthenic acids, and phenols on the freshwater crustacean Daphnia magna. Veldre (63) listed the threshold concentrations of waste waters from tar distillation and phenol fractionation plants to freshwater organisms.

Effects of Detergents

There is little doubt that detergents, or emulsions of detergents and oil in water, have a more severe effect on aquatic forms of life than oil alone. Because of the wide diversity of emulsifiers, their effects are manifold. Each emulsifier, under conditions which are seldom static, may be expected to affect various species at different concentrations in a number of ways.

Hettche (22) discussed detergents from the biological standpoint.

Heinz and Fischer (19) evaluated the potential effects of detergents on fish and microorganisms, and included a list of 176 references. Comprehensive reviews concerning detergents in waters, with extensive reference lists, are provided by the Organization for Economic Cooperation and Development (1) and the U. S. Public Health Service. (2)

Pohl and Svee ⁽⁴⁹⁾ considered that all concentrations of a synthetic detergent of the alkylbenzenesulfonate, or ABS, type were harmful to life above 2 ppm and that concentrations of 20 ppm or more were lethal even to relatively resistant freshwater organisms. Mann⁽³¹⁾ examined oilbinding materials for their effect on fish and animals forming fish food and found many of them to be harmful.

Much emphasis in recent years has been focused on developing biologically degradable detergents on the assumption that they cause less damage. Pitter $^{(48)}$ found that alkyl sulphates were resistant and alkyl benzene sulphonates were susceptible to biological decomposition; the presence of a branched chain on the molecule reduces degradability of both compounds. Pitter $^{(47)}$ showed that high-molecular polyoxyethylene detergents resisted degradation and biological hydrolysis of the sulphate group and partially retained their anionic character, but that low molecular nonsulphated types were readily decomposed. Swisher $^{(59)}$ described the biodegradation process of linear alkylate sulphonates. Tarring $^{(60)}$ discussed the undesirable effects caused by nonbiodegradable synthetic detergents. Simonis $^{(56)}$ reported on new detergents with properties of complete degradability and high purification efficiency at low temperatures. Some syndets that inhibit and resist biological decomposition, and some that were readily oxidized are evaluated by Sheets and Malaney. $^{(55)}$

Freshwater Fauna. One of the most popular invertebrates for testing toxicity levels of synthetic detergents in freshwater is the copepod Daphnia magna. Degens et al. (11) found that Daphnia, and also tadpoles and sticklebacks, were killed by 24 hr exposure or more to 5 ppm of alkyl aryl sulphonate. Freeman (15) conducted bioassays with sodium sulfonates and found a 50% mortality of Daphnia on 100 hr exposures to various concentrations ranging from 12 to 3380 ppm. Sodium benzene sulfonate was among the least toxic of 10 different compounds, and the more complicated the ring structure the more toxic the compound. Mann (33) noted that Daphnia were first damaged by a detergent at concentrations of 5 ppm, but the copepod adapted to the toxicity when concentrations were slowly increased. Nehring (40) presented toxicity thresholds of flotation reagents for Daphnia and for the amphipod Gammarus. Cabejszek et al. (6) reported that Sulfapol-50 (containing 50% sodium dodecyl benzene sulphonate) killed Daphnia in 24 hr at doses of 4 to 6 mg/liter.

Dowden (13) conducted bioassays with two waste-oil emulsifiers (foaming and white emulsified) on <u>Daphnia</u> in test media of the emulsifier, crude oil, and equal parts emulsifier and crude oil. Crude oil was found

to be relatively nontoxic, and its toxicity was attributed to entrapment of test animals at the surface of the test solutions. The foaming emulsifier was more toxic when combined with crude oil, and was attributed to intimate contact of the emulsified oil with <u>Daphnia</u>. The white emulsoid was most toxic; there was no difference in Tl_m between the emulsifier and the emulsifier mixed with crude oil.

Optiz and Loeser (45) established the median lethal concentrations of dodecyl and tetrapropylene benzene sulfonates for tadpoles at 21.6 and 7.6 mg/liter, respectively. Mann (34) described the toxic effects of alkyl aryl sulfonate on the oligochate Tubifex, the dipteran larvae Chironomus, and the isopods Carinogammus and Asellus; tubificids were the most resistant and chironomids the most sensitive. He reported that anionic and nonionic detergents, and washing and cleaning agents containing them, were lethal at concentrations from 10 to 25 ppm. Mann (32) also found that increases in temperature and decreases in oxygen increased the toxicity of the compounds. Leibmann (25) stated that synthetic detergents damage lower organisms and cold-blooded organisms considerably more than warmblooded organisms.

Roberts (53) observed high mortalities of the amphipod Gammarus after 7 days exposure to a commercial anionic detergent at 7.5 ppm; even mortality rates at 2.5 to 5.0 ppm were higher than in the controls.

Veger (62) established various maximum permissible concentrations of the detergent RA Decontaminator, as well as its individual components, to ten freshwater organisms. Surber and Thatcher (58) found that amphipods and isopods were reduced in numbers when exposed to 10 mg/liter of ABS for two or more weeks. The extreme toxicity of various flotation reagents for Tubifex and Asellus were determined by Sindelar and Marvan. (57)

Aquatic insects also indicate the toxicity of detergents. Hepworth, ⁽²¹⁾ who investigated the effects of a synthetic, nonionic, nonsulfonated detergent (Kyro-Ero) on insect larvae, established the 96-hr LD₅₀ (lethal to 50% of the population) values of 5.2, 4.7, and 4.9 ppm for the nymphs of mayflies, stoneflies, and damselflies, respectively. Diptera larvae, chiefly Tendipedidae, withstood 10 ppm

without mortality. Surber and Thatcher (58) found that mayfly nymphs died after exposure to 16 mg/liter or more of ABS for 10 days, while hydropsychid larvae were more resi tant and survived 10 days at 32 mg/liter. Henson and Henson observed that mosquitoe larvae were unable to survive in water containing detergents in concentrations greater than 62.5 ppm; failure to remain affoat for respiratory purposes was attributed to the lowering of surface tension.

Marine Fauna. Little experimental work has been done on the effects of detergents on marine macroinvertebrates. Gross observations in recent years following application of detergents to remove oil spills indicate extensive damage to coastal fauna. George (16) believed that oil spilled in Milford Haven was nontoxic to polluted organisms, but that emulsifiers used to clean contaminated shores caused heavy mortalities. He concluded that since oil films are removed fairly quickly by natural processes, the use of emulsifiers seemed wasteful and unnecessary. Nelson-Smith (38) considered emulsifiers by themselves to be very toxic. He stated, "In addition to this direct toxic effect, emulsifiers exert a profound indirect influence upon shore life. By thinning the oil. they enable it to spread beyond the original limits of pollution; in making it miscible with water, they enable it to penetrate crevices and suspend throughout the water of a rock-pool the oil-film which previously only covered its surface. Emulsified oil, coming into contact with living animals, clings to the slimy surfaces of gills and gut which untreated oil cannot wet. Furthermore, some of the droplets of suspended oil washed into the sea from an emusifier-sprayed shore or dispersed from a floating oil slick fall within the size range of particles which are gathered as food by such filter-feeders as the very susceptible bivalve molluscs."

Glude and Peters (18) stated that 500, 000 gal, of detergents were used at sea and over 2 million gal, ashore after the TORREY CANYON spill. According to them, the detergent BP-1002 has been found to be toxic to the marine annelid Sabellaria at a concentrations of 1 ppm; 5 ppm of this detergent will kill 50% of the larvae of the barnacle Eliminius in a short time. Furthermore, the three principal components of BP-1002 are

kerosene (85%), coconut oil (3%) and surfactant (12%). Although each component was somewhat toxic, the kerosene fraction was by far the most harmful. Spooner (69) reports that this detergent was lethal in concentrations of 1 to 10 ppm to barnacle larvae, shrimp, and a species of worm larvae; it was vastly more harmful than the oil itself. Potta, Gage, and Forster (70) report observations by offshore diving of the littoral fauna after the TORREY CANYON incident. At one location a quarter of a mile offshore, brittle stars and sea urchins were affected. They concluded that there was without doubt a considerable toxic effect at over 8 fathoms depth from the mixture of oil and detergent.

Nelson-Smith⁽³⁸⁾ considered the most efficient use of emulsifiers to be the least damaging biologically. Efficient use required treatment of the oil at sea where the emusifier can be readily carried and sprayed on oil slicks, and the emulsion thus formed is dispersed in a large volume of water. Nelson-Smith⁽³⁹⁾ also reviews the literature concerning the toxicity of oils and emulsifiers in the marine environment, and summarizes his observations of periodic oil contamination over several years in Milford Haven, England.

A general account of the effects of oil and emulsifier following the wreck of the TORREY CANYON is given by O'Sullivan and Richardson. (46, 71)

In areas contaminated only by oil, animal life generally remained normal and healthy, whereas high mortalities occurred where detergents were used. These conclusions were basically substantiated by Williams, (66)

Nelson-Smith, (39) and Glude and Peters. (18)

Manwell and Baker⁽⁷²⁾ felt that most of the detergent applied to remove oil after the TORREY CANYON was at best a waste - possibly of 5,000,000 British Pounds.

Repopulation

Bryan⁽⁷³⁾ reported that when a rocky shore about one-quarter mile long was treated with about 35,000 gal of the detergent BP1002 over several days on each rising tide following the TORREY CANYON disaster the effects were: 1) to kill all crustaceans except barnacles, 2) to kill all mollusks except Nucella, Monodonta, and Littorina littorea, which were knocked off the rocks but climbed back later, 3) to kill all red seaweeds except Corallina, and 4) kill all shore fish and cchinoderms.

Some worms and anenomes, such as <u>Tealia</u>. <u>Actinia</u>, and <u>Anenomia</u> survived. Offshore, the effects on <u>Ensis</u>, the razor clam, and <u>Echimocardium</u> extended for about one mile to around the 10 fathom line. The absence of fish was also very obvious.

Most of the shores have now begun to recover, but because all the limpets were killed, the seaweeds have grown unchecked. In the summer of 1967, all the shores were covered with Enteromorpha, and this is now being replaced by a large growth of the fucoid seaweeds. Barnacle settlements have covered the areas previously occupied by limpets. Larvel crabs and many small crustaceans have reappeared along with a few of the larger crabs and small fish. The gastropod molluses that survived showed a marked ridge on the shell where growth was stopped.

Literature Cited Concerning Oil Pollution and Other Life Forms

- 1. Anonymous. "The Pollution of Water by Detergents," Org. Econ. Coop. Devel., Paris, 86. 1964.
- Anonymous. <u>Bibliography on Synthetic Detergents in Water and Wastes Including Analytical Methods and Physiological Effects</u>.
 U. S. Public Health Service, R. A. Taft San. Eng. Center, Cincinnati, Ohio, 91 pp. 1964.
- 3. Belikhov, D. V. "Sanitary and Biological Studies of the Volga River Before Its Regulation Near Mogutovakaya Mountain," lst Sci. Tech. Meeting on the Study of the Kuibyshev Reservior. No. 3 Kuibyshev 23. 1963. Biol. Abst. vol. 46, p. 73951, 1965.
- 4. Boswell, J. L. Report on Experiments to Determine the Effect of a Surface Film of Crude Oil on the Absorption of Atmospheric Oxygen by Water, Texas A and M. Res. Found., Proj. 9, Report (Mimeo), 6 pp. 1950.
- 5. Brown, S. O. and B. L. Reid. Report on Experiments to Test the Diffusion of Oxygen Through a Surface Layer of Oil, Texas A and M Res. Found., Proj. 9, Report (Mimeo), 5 pp. 1950.
- 6. Cabejszek, I., J. Just, J. Luczak and J. Maleszewska. "Influence of Sulfapol-50 on Physico-Chemical Properties and Biocenosis of Water," Gaz Woda Tech. Sanit. vol. 37, pp. 53-57. 1963. Water Poll. Abs. (Brit.), vol. 38, p. 1372. 1965.
- Chambon, M. "Considerations on the Pollution of River Waters and the Role of Synthetic Detergents," <u>Eau</u>, vol. 48, pp. 329-336. 1961.
- 8. Chipman, W. A. and P. S. Galtsoff. Effects of Oil Mixed with Carbonized Sand on Aquatic Animals, U.S.F.W.S., Spec. Sci. Rept. Fisheries, vol 1 pp. 1-52, 1949.
- 9. Clendenning, K. A. and W. J. North. "Effects of Wastes on the Giant Kelp, Macrocystis pyrifera," Waste Disposal in the Marine Environment, Proc. 1st Int. Conf., Pergamon Press, N. Y., pp. 82-91. 1960
- 10. Crosby, E. S., W. Rudolfs, and H. Heukelekian. "Biological Growths in Petroleum Refinery Waste Waters," Ind.-Eng. Chem., 46(2), pp. 296-300. 1954.
- Degens, I. P. N., Jr., H. Vander Zee, J. D. Kommer. and H. A. Kampkuis. "Synthetic Detergents and Sewage Processing. The Effect of Synthetic Detergents on Certain Water Fauna," J. and Proc. Inst. Sew. Purif., Part I, pp. 63-68, 1950.
- 12. Diaz-Piferrer, M. "The Effects of an Oil on the Shore of Guanica, Puerto Rico," Deep Sea Research, 11(5), pp. 855-856, 1964.

- Dow-len, B. C. "Toxicity of Commercial Waste-Oil Emulsifiers to Daphnia magna," J. Water Poll. Cont. Fed. 34(10), pp. 1010-1014.
- 14. Downing, A. L. and A. G. Truesdale. "Some Factors Affecting the Rate of Solution of Oxygen in Water," J. Appl. Chem., London, vol. 5, pp. 570-581, 1955.
- 15. Freeman, L. "Toxicity Thresholds of Certain Sodium Sulfonates for Daphnia magna," J. Water Poll. Cont. Fed., 25(11), p. 1331. 1953.
- 16. George, M. "Oil Pollution of Marine Organisms," Nature 192(4804), p. 1209, 1961.
- 17. Gilet, R. "Water Pollution in Marseilles and its Relation with Flora and Fauna," Waste Disposal in the Marine Environment, Proc. 1st Intl. Conf., Pergamon Press, London, pp. 39-56, 1960.
- 18. Glude, J. B. and J. A. Peters. Observation on the Effect of Oil from the Tanker TORREY CANYON and Oil-Control Measures on Marine Resources of Cornwall, England and Brittany, France. Unpub. Rept. to Director, Bur. Comm. Fish., Washington, D. C., June 1967. (Mimeo) 7 pp. 1967.
- 19. Heinz, H. J. and W. K. Fischer. "Detergents in Water and Sewage," Fette Seif. Anstrichm, vol. 64, p. 270. 1962. Public Health Eng. Abst., vol. 43, p. 1531. 1963.
- 20. Henson, J. and R. Henson. The Action of Detergents on Aquatic Insects. Publ. Health, Johannesburg, vol. 18, p. 11. 1955.
- 21. Hepworth, W. G. Toxicity of the Non-ionic Detergent Kyro-Ero to Brook Trout, Rainbow Trout, and Nymphal Mayflies, Stoneflies, Damselflies, and Larval Midges. Fed. Aid Fish Wildlife Rest. Wyoming FW-3-R-8, Work Plan No. 9, Analysis No. 21, pp. 40-41. (mimeo). 1951.
- 22. Hettche, H. O. "Detergents from the Biological Standpoint,"

 Detergents and Their Influence on Water Supply, River Water, and

 Sewage. Gas-u. Wasserfach, vol. 101, pp. 501-502, 1960.
- 23. Klinke, H. R. "Effects of Oil and Tar Products in Water on the Fish Organisms," Munch. Beitr., vol. 9, p. 75. 1962. Water Poll. Abs., 37(6), p. 1018. 1964.
- 24. Lambin, S., C. Carrere and M. B. DeValamont. "Biologic Degradation of Synthetic Detergents by the Microbial Flora of Liquid Waste," Annls. Pharm. Fr., vol. 24, pp. 161-166, 1966.
- 25. Leibmann, H. "Effect of Oil and Detergents in Water on Natural Selfpurification," Munch. Beitr. Abwass.-, Fisch.-u. Flussbiol, vol. 9, pp. 11-13. 1962. Water Poll. Abs. (Brit.), vol. 37, p. 1376, 1964.

- 26. Mackin, J. G. Report on a Study of the Effect of Application of Crude Petroleum on Saltgrass, Distichlis spicata (L.) Greene, Texas A and M Res. Found., Project 9 Report, (Mimeo)., 5 pp. 1950.
- 27. Mackin, J. G. and A. K. Sparks. A Study of the Effect on Oysters of Crude Oil Loss from a Wild Well. Publ. Inst. Mar. Sci., U. Texas, vol. 7, pp. 230-261, 1962.
- 28. Malacea, I., V. Cure, and L. Weiner. "Contributions to the Knowledge of the Noxious Action of Oil, Naphthenic Acids and Phenols on Certain Fish and the Crustacean Daphnia magna Strauss," Stud. Prot. Epur. Apel., vol. 5, pp. 353-397, 402-405. 1964. Water Poll. Abst. (Brit.), 38(9), p. 1565. 1965.
- 29. Malina, J. F. "Toxicity of Petrochemicals in the Aquatic Environment," Water and Sewage Works 111(10), pp. 456-460. 1964.
- 30. Manganelli, R. and E. S. Crosby. "Effect of Detergents on Sewage Microorganisms," J. Water. Poll. Cont. Fed., 25(3), p. 262. 1953.
- 31. Mann, H. "Examination of Oil-Binding Materials for Their Effect on Fish and Animals Forming Fish Food," Fischwirt, vol. 6, pp. 1-4. 1966.
- 32. Mann, H. "The Importance of Synthetic Washing Agents (Detergents) to Fisheries," Fischwirt, vol 12, pp. 97-101, 1962, Water Poll. Abs. (Brit.), vol. 37, p. 1010, 1964.
- 33. Mann, H. "The Effect of Various Disinfectants on Fish and Animals Serving as Fish Food," Z. Fisch., vol. 6, pp. 134-140, 1958.
- 34. Mann, H. "The Action of Sub-surface Washing Agents on Fish and Animals Forming Fish-Foods," Arch. Fischwiss., vol 6, pp. 131-137, 1955. Water Poll. Abs. (Brit.), vol. 28, pp. 393. 1955.
- 35. McCauley, R. N. "The Biological Effects of Oil Pollution in a River," Limnol. Oceanogr, 11(4), pp. 475-486. 1966.
- McKee, J. E. Oily Substances on Their Effects on the Beneficial Uses of Water, Publ. No. 16, State Water Poll. Control. Bd. Sacramento, Calif., 72 pp. 1956.
- 37. Minter, K. W. Standing Crop and Community Structure of Plankton in Oil Refinery Effluent Holding Ponds. Ph. D. Thesis, Okla. State Univ., 104 pp. Water Poll. Abs., (Brit.), p. 1182, 1965.
- 38. Nelson-Smith, A. "Oil, Emulsifiers and Marine Life," Conservation and the TORREY CANYON, J. Devon Trust for Nature Conservation (Suppl.), July, 1967, pp. 29-33.

. .

- 39. Nelson-Smith, A. "The Effects of Oil Pollution and Emulsifier Cleansing on Shore Life in South-West Britain," J. Appl. Ecol., vol. 4, p. 2, 1967, (in Press).
- 40. Nehring, D. "The Action of Flotation Reagents on Fish and Fishfood Animals," Z. Fischeri, 11(3/4), p. 313. 1963. Chem. Abs., vol. 60, p. 7204. 1964.
- 41. North, W. J. "TAMPICO, A Study of Destruction and Restoration," Sea Frontiers, vol. 13, pp. 212-217. 1967.
- North, W. J. An Investigation of the Effects of Discharged Wastes on Kelp, Calif. State Water Qual. Cont. Bd., Publ. No. 26, 176 pp. 1964.
- 43. North, W. J. Successive Biological Changes Observed in a Marine Cove Exposed to Large Oil Spillage. Univ. Calif., Inst. Mar. Res., Ref. 61-6, pp. 1-33. 1961.
- 44. North, W. J., Neushul, Jr. and K. A. Clendenning. "Successive Biological Changes Observed in a Marine Cove Exposed to a Large Spillage of Mineral Oil," Pollutions Marines par les Microorganismes et les Products Petroliers. Comm. Intl. Pour L'Exploration Scientifique de la mer Mediterranee, Symposium de Monaco, April, 1964, pp. 335-354. 1965.
- 45. Opitz, K. and A. Loeser. "The Effect of Alkylbenzene-sulfonates on Tadpoles," Experientia, 20(5), pp. 277-278. 1964. Chem. Abs., vol. 61, p. 1015. 1964.
- 46. O'Suilivan, A. J. and A. J. Richardson. "The TORREY CANYON Disaster and Intertidal Marine Life," Nature 214:448, pp. 541-542.
- 47. Pitter, P. "Biological Decomposition of Sulphated and Nonsulphated Non-ionic Detergents," Prum. Potravin, vol. 15, pp. 649-650, 1964.
- 48. Pitter. P. "Surface-active Agents in Waste Waters. V. Alkyl Sulphates Resistant and Alkylbenzenesulphonates Susceptible to Biological Degradation," Sb. Vys. Sk. Chem-Technol. Praze Technol. Vod., vol. 2, pp. 19-32, 1963.
- 49. Pohl, B. and J. Svec. "Detergents of the ABS Type and Our Waters," Cslka Hyg., vol. 5, pp. 471-475, 1960.
- 50. Reimann, K. "Harmfulness of Oil and Tar Products to Lower Water Organisms," Munch. Beitr. Abwass.-, Fisch.-u. Fluss Biol, vol. 9, pp. 60-72. 1962.

- 51. Reish, D. J. "The Effect of Oil Refinery Wastes on Benthic Marine Animals in Los Angeles Harbor, California," Pollutions Marines par les Microorganismes et les Produits Petrollers.

 Comm. Intl. Pour L'Exploration Scientifique de la mer Mediterrance, Symposium de Monaco, (April, 1964), pp. 355-361, 1965.
- 52. Reish, D. J. and H. A. Winter. The Ecology of Alamitos Bay, California, with Special Reference to Pollution, Calif. Fish and Game 40(2), pp. 105-121, 1954.
- 53. Roberts, F. W. "Some Residual Effluent Problems," Water-Sanit. Eng., vol. 5, pp. 13-15. 1954.
- 54. Rodina, A. G. "Bacteria as Food of Aquatic Animals," Priroda, vol. 38, pp. 23-26. 1949.
- 55. Sheets, W. D. and G. W. Malaney. "The C.O.D. Values of Syndets, Surfactants, and Builders," Proc. Ind. Waste Conf. 11th Conf., Purdue Univ., 1956, pp. 185-196. 1957.
- 56. Simonis, H. "On Biologically Decomposable Detergents," <u>Dechema-Monogr.</u>, 52(902), pp. 125-130. 1965. Finish, Saulqau/Wurtt, 12(1), p. 29.
- 57. Sindelar, Wl. and P. Marvan. "Toxicity of Floatation Reagents for Aquatic Organisms," Bergakademie 17(2), pp. 103-107. 1965. Chem. Abst. 63(3), p. 3369b. 1965.
- 58. Surber, E. W. and T. O. Thatcher. "Laboratory Studies of the Effects of Alkyl Benzene Sulfonate (ABS) on Aquatic Invertebrates "Trans. Amer. Fish Soc. 92(2) pp. 152-160. 1963
- 59. Swisher, R. D. "The Biodegradation Process in Linear Alkylate Sulphonate," 54th Nati. Meeting, Am. Inst. Chem. Engineers, September, 1962. 12 p. 1964.
- 60. Tarring, R. C. "The Development of a Biologically Degradable Alkylbenezenesulphonate," Proc. 2nd Int. Conf. Water Pollut. Res., Tokyo, 1964, vol. 1, pp. 113-149. 1965.
- 61. Tubb, R. A. and T. C. Dorris. "Herbivorous Insect Populations in Oil Refinery Effluent Holding Ponds Series," Limnol. and Oceanog. 10(1), pp. 121-134. 1965.
- 62. Veger, J. "Toxic Effect of Waste Water Containing the Detergent R. A. Decontaminator Upon Water Organisms," Vodi Hospodasrtve, vol. 12, pp. 172-173. 1962. Chem. Abs., vol. 57, p. 10947. 1962.

- 63. Veldre, I. "Toxological Characteristics of Shale Waste Waters," Rybn. Khoz. Unutr. Vodemomov Latv. SSR, Sb., pp. 55-59. 1963. Chem. Abs., vol 61, p. 14345. 1964.
- 64. Voroshilova, A. A. and E. V. Dianova. "Bacterial Oxidation of Oil and Its Migration in Natural Waters," Mikrobiologiya, vol. 19, pp. 203-210, 1956.
- 65. Wiebe, A. H. "The Effect of Crude Oil on Freshwater Fish," Trans. Amer. Fish. Soc., vol. 65, pp. 324-331. 1935.
- 66. Williams, J. K. "Detergent and Wildlife," TORREY CANYON, pp. 207-208, 1967. Birds 1(10), pp. 201-212.
- 67. ZoBell, C. E. "The Occurrence, Effects, and Fate of Oil Polluting the Sea," Intl. Conf. on Water Poll. Res., London Sept. 3, 1962, Sect. III, 27 pp.

Addenda

- 68. Copland, W. O. TORREY CANYON Pollution, J. Devon Trust Nature Conservation (Suppl.), July, 1967, pp. 8-11. July 1967.
- 69. Spooner, M. F. Biological Effects of the TORREY CANYON Disaster, J. Devon Trust Nature Conservation (Suppl.), pp. 12-19. July 1967.
- 70. Potts, G., J. Gage, and F. Forster. Diving Studies on the TORREY CANYON Oil Pollution, J. Devon Trust Nature Conservation (Suppl.), pp. 22-24. July 1967.
- 71. O'Sullivan, A. J. and A. J. Richardson. The Effects of the Oil on Intertidal Marine Life, J. Devon Trust Nature Conservation (Suppl.), pp. 34-38. July 1967.
- 72. Manwell, C. and C. M. Baker. Oil and Detergent Pollution, J. Devon Trust Nature Conservation (Suppl.), pp. 34-38. July 1967.
- 73. Bryan, G. W. Personal Communication, Marine Biological Association of The United Kingdom. Plymouth. England. November 1967.

6.5 BIOASSAY OF DETE GENTS

1

Because of the charging composition of the oil and detergent in aerated seawater and the e of detergents with different chemical compositions, chemical methods of detection could not be used following the TORREY CANYON: saster. Biological methods are not very accurate, but reasonable detergent concentration data were obtained with shrimps for concentrations of between 2 and 100 ppm of the detergent BP1002. (1)

The animals to be tested were sealed in 200 ml bottles of the seawater to prevent evaporation of the volatile components, and the time taken for the shrimps to turn over was measured. From a standard curve, the concentration of detergent or solvent in the sea, in terms of BP1002 could be estimated.

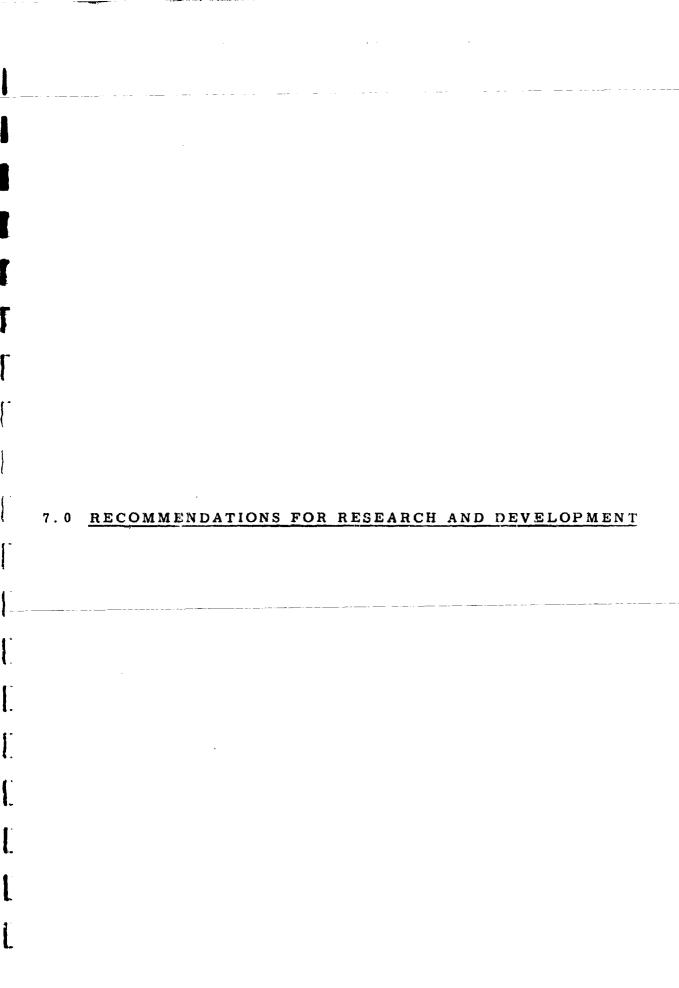
In toxicity tests, organisms were exposed to different concentrations of detergents for 24 hr and were then placed in clean seawater for recovery.

Shrimps were the most sensitive of the larger crustaceans and were killed at 2 ppm. Twenty-five ppm was required to kill the crab Carcunis. Alternately barnacles seemed to be very hardy, and in some instances must have withstood almost pure detergent for some time. Of the molluscs, the sublittoral bivalves such as the razor clam Ensis were very sensitive and were killed by 0.5 ppm. Limpets were killed by 5 ppm, but Nucella, Monodonta, and Littorina littorea survived up to 50 to 100 ppm, confirming the field observations. Starfish were killed by about 10 ppm and the sublittoral heart urchin, Eshinocardium, was killed by 0.5 to 1.0 ppm.

Fish were probably affected by about 10 ppm, but the polychaete worms, Nereis, withstood 25 ppm.

The most sensitive seaweeds were the filamentous reds, which were killed at about 10 ppm. Many of the fucoids however seemed to be able to withstand almost 100% detergent.

⁽¹⁾ Bryan, G. W. Personal Communication, Marine Biological Association of the United Kingdom, Plymouth, England. November 1967.



7.0 RECOMMENDATIONS FOR RESEARCH AND DEVELOPMENT

As a result of this study, several areas were identified where advance planning and research and development can be expected to result in improved capability for preventing and combating oil spillage and for minimizing its consequences. These areas are summarized below, and in several instances, the recommendations apply to other hazardous cargoes.

7.1 GENERAL

7.1.1 Contingency Planning Activities

Contingency plans for coping with major oil and other hazardous cargo disasters should be undertaken with a systems analysis approach. Planning activities should be focused on specific geographical areas and be conducted in concert with Federal, state, and local authorities and industries. These contingency plans should be specifically directed at:

- Providing area authorities with advance estimates of probability of accidents including consideration of type of cargo, severity, location, and path of pollutant
- Reviewing sectors of the area economy and resources, e.g., fisheries, recreation, and water supplies that might be affected and how these might dictate or restrict control measures
- Establishing a warning and communication network to be activated in the event of an emergency, including an inventory of equipment and supplies and their sources, and sources of pertinent real-time environmental data that would be required in the event of an emergency
- Providing a rational basis for stockpiling control or restoration equipment and materials
- Establishing specific plans of action for selected situations of higher estimated probability and severity
- Identifying key precautions that should be taken in advance.

Such analyses might bear some resemblance to porting studies conducted in connection with the N. S. SAVANNAH and would take into

account such area environmental factors as prevailing winds, currents, hazards to navigation, traffic density, demography, etc. Such planning should not be static but should include projection into the future and with provision for periodic updating.

Although this study has been specifically directed at oil spillage, it seems very appropriate to consider contingency planning in the broader sense to embrace other hazardous cargoes. Much of the information required for contingency planning for one potential hazard is equally necessary for other cargoes.

7.1.2 Oil and Other Hazardous Materials Information Center

The increasing transport of hazardous commodities by land, sea, and air; the increasing density of traffic and size of population centers; the increasing bulk of individual shipments; and the complex interrelationships of the hazardous materials with the environment and natural resources (e.g., water supplies and air sheds); point to an increasing need for a hazardous materials information and evaluation center oriented specifically to transportation problems: i.e., mobile sources of pollution.

In this study, which was restricted to oil spillage alone, the large volume of available pertinent information came as a surprise, and it became increasingly apparent that some form of continuously maintained information and technical analysis center would be a highly desirable contribution to the national posture in regard to transport of hazardous materials of which oil is perhaps the least. For example, in several instances in this study, unpublished or limited distribution material provided information that changed or modified the recommendations presented in this report and uncovered areas of inadequate knowledge.

Four specific areas should be included within the scope of such an information center:

- 1. Definition and classification of hazardous cargoes
- 2. Development and interpretation of transportation statistics as they relate to the cargoes and potential hazards en route

- 3. Technical review and assessment of the commodity per se, packing and handling criteria, mode of transport, potential compatibility or synergistic effects, etc.
- 4. Resource and environmental effects and means for limiting the consequences.

To be fully effective, such a center must have more than a collection and archiving function. Capability should be built-in to provide for analysis and interpretation.

The recommended center would necessarily have to draw an expertise in a large number of disciplines: chemistry, oceanography, hydrology, meteorology, toxicology, ecology, engineering, biology, economics, etc. The center must maintain an up-to-date awareness of all aspects of hazardous cargo accidents—their prevention, control and effects, and the restorative actions that can be taken. Specifically, the recommended center could maintain an up-to-date and running appraisal of statistics, technology, and practices in the following areas:

- 1. Classification of hazardous materials
- 2. Compatibility with other cargoes
- 3. Frequency, routes, density, etc., of transport and mode
- 4. Special precautions and practices
- 5. Packaging technology
- 6. Combinatorial circumstances which could result in accidents, e.g., unfortuitous situations to be avoided
- 7. In-transit monitoring needs and potential
- 8. Control procedures and actions that could be effected to limit consequences
- 9. Water or other economic resources likely to be effected, including extent of damage as a function of quantity of material and time since an accident
- Meteorological and hydrological phenomenon as they pertain to spread of hazardous materials

- 11. Ecological and biological effects of hazardous material release and the countermeasures employed
- 12. Transferrable technology from other fields applicable to hazardous material transport.

The hazardous materials information center would, in addition to the above continuing role, provide technical expertise and backup in the following areas:

- 1. Assist in the preparation of packaging, shipping, handling, and routing criteria
- 2. Participate in special hazards reviews
- 3. Provide technical basis for contingency planning activities
- 4. Provide a capability for quick response of appropriate scientific and technical disciplines to emergency situations
- 5. Recommend, where appropriate, specific planning and research and development activities.

The center should be established in such a manner as to be readily accessible to appropriate Federal agencies, state and local governments, and manufacturers, carriers and insurers of hazardous materials.

7.2 PREVENTION OF OIL SPILLAGE

7. 2. 1 Governmental and Regulatory Body Studies

Cansiderable private and government activity following the TORREY Canyon incident has been aimed at establishing study programs for future regulation. Of greatest importance is the potential work of the international Maritime Consultative Organization subcommittees, particularly the Maritime Safety Committee, which has expanded its activities to include studies of gross oil pollution in addition to its normal agenda on containment of hazardous cargoes. The first pertinent meeting of this group will be held in January 1968. At the time of this writing, however, no action of significance has been taken by regulatory or governmental agencies.

7.2.2 Maneuverability

Maneuverability is considered here as a primary means for avoiding collision and grounding in emergency conditions. Accordingly, the following observations and studies are pertinent to the overall problem.

Backing Power

Data given in Reference 29 of Section 3.1 demonstrates that steam turbine propelled, single screw U.S. flag tankers with displacements ranging from 25,000 to 77,000 tons can be expected to stop in 8 1/2 to 9 ship lengths from the full ahead condition. Further, periods of 5 1/2 to 9 min will be required to execute this maneuver from the time the crash stop order is given.

By contrast, the 144,000 dwt, combination oil/bulk vessel CEDROS, described in Reference 132 of Section 3.1, required 10 1/2 ship lengths and over 11 min to stop from an initial speed of 18 knots.

The geared steam turbines installed in the above ships are fitted with astern elements with a capability of about 80% full ahead torque and 50% full ahead rpm, i.e., about 40% of full ahead power. The time required to obtain full astern revolutions, from the full ahead condition, is on the order of 1 min.

At the time of this writing, no comparable data was available for direct reversing diesel engines. The model experiments reported in

Reference 3 of Section 3.1 indicate that crash stop characteristics of the diesel ship may be somewhat better, probably because full astern power is available.

It has been shown that tanker sizes have grown at a far greater rate than the installed power. Hence, the stopping ability has been reduced significantly, with the obvious reduction in ship maneuverability. Accordingly, the following studies are suggested:

- Extensive study of backing characteristics of existing vessels, particularly with respect to known casualties.
- Establishment of minimum recommended or mandatory standards defining acceptable values of ahead reach and time to execute the crash stop maneuver, as measured on standardization trials. This will effectively establish minimum acceptable values of astern powers for the various types of power plants.
- Study of effects of propeller type on stopping characteristics. The model studies discussed in Reference 3 of Section 3.1, for example, indicate that the controllable pitch propeller is superior in this characteristic to fixed pitch propellers. Further, it is clearly demonstrated that propeller systems, e.g., fixed pitch, controllable pitch, contra-rotating and ducted fixed pitch, are best matched to particular prime movers to obtain optimum astern characteristics.
- Study of relative characteristics of various transmission systems. Where geared or electric drive systems are applicable, various reversing methods are available. In the extreme example, the 20,000 shp diesel-electric plant of a modern icebreaker can be stopped from full ahead to 0 rpm in 10 sec and full ahead to full astern in about 20 sec. The potential gains from the various systems should be evaluated by an analysis of the rpm-torque-thrust characteristics over the entire crash stop time sequence.
- Study of auxiliary braking devices, including the following:
 - 1. Shaft brake systems, mechanical or other.
 - 2. Hydrodynamic-Various schemes have been considered in the past, including a Japanese rudder design with hinged leaves

which open to form flat braking surfaces at 90° to the direction of motion. Other concepts may be considered, including adaptation of thruster systems, active rudders, etc.

Steering and Directional Control

The second second address.

Table 3.1-4 summarizes tactical diameters of a few tank vessels, ranging from the early 19,000 dwt tankers to the CEDROS and NISSHO MARU, each over 100,000 dwt. Tactical diameters have remained essentially constant in this limited sample. However, in view of the greatly increased sizes and relatively reduced installed power, consideration should be given to improving maneuvering characteristics at sustained sea speeds as well as at reduced speed conditions. Accordingly, the following studies are suggested:

- Extensive study of maneuvering characteristics of existing ships, with particular reference to casualty records.
- Establishment of minimum standards for control, including turning rate, turning circles, etc., as determined by standardized trials procedures.
- Study of rudder design. For the large single screw tanker particularly, consideration should be given to rudder designs other than the current standard horn type rudders or conventional, closed stern, fairform rudders, in order to improve characteristics at high rudder angles and at low maneuvering speeds. The various configurations that might be studied include active rudders (per the Pleuger design), biplane and triplane rudders, flapped rudders, Kort nozzle rudders, etc.
- Thruster design. Various bow and stern thruster systems have been developed, some well over 1000 hp in size. Applicability to the large tanker, as an augment to the steering system, should be considered. The following systems are applicable:
 - 1. Ducted bow and/or stern thrusters, using reversible fixed pitch or controllable pitch propellers. Such systems are the most common in use on large, full-block ships. Consideration should be given to use of two ducted units in tandem where existing units are inadequate in size.

- 2. Active rudders. Such units have been installed on relatively small vessels, e.g., oceanographic ships or small cargo vessels. The particular advantage is the ability to apply thrust over a range of directions and the availability of the system as a secondary means of propulsion in the event of failure of the main system.
- 3. Jet thrusters. Use of the tanker ballast system as a source of energy for powering fixed stern thrusters has been proposed and is the subject of a Japanese patent. While probably not as effective as the ducted propeller, the system is relatively inexpensive and uses existing pumping machinery.
- 4. Retractable, trainable bow and/or stern propellers. Such systems have been installed in relatively small vessels such as the U.S. Navy AGOR oceanographic vessels. While relatively expensive, such devices can exert a thrust over 360° and can serve as a secondary means of propulsion.

7.2.3 Arrangement Modifications

Studies suggested here would be directed toward structural protection against collision and grounding. It will be clear that modifications in this direction will generally involve increased ship cost, increased light ship weight, hence, reduced cargo deadweight capacity and reduced cargo cubic capacity. These disadvantages must be weighed against the gains in ship safety and reduced probability of losing cargo oil in event of cargo tank rupture.

Collisions Protection

The direct approach is the provision of a structural barrier at the ship side, in way of the cargo tanks. This outer space, while lost to cargo capacity, is available for clean ballast. This loss in cubic capacity is important when light cargoes, such as gasoline, are carried and the ship must be larger to carry a given amount of deadweight.

One effort in this direction is described in References 52 and 90 of Section 3.1 with respect to design of the tanker FORTUNA. As discussed

earlier, the conventional port and starboard wing bulkheads are located well outboard, and the wing spaces are used exclusively for the carriage of clean water ballast. The ship was built deeper than normal to compensate for the loss in cubic capacity. The effectiveness of this arrangement was demonstrated in a collision in which one ship of the class survived a broadside collision without breaching the cargo tanks. In very large ship sizes, this arrangement would probably require the installation of an additional longitudinal bulkhead on the centerline.

Other protective systems could be studied, including the fitting of heavy longitudinal guards or fenders outboard of the side shell, using built-up sections, "blister" configurations, etc.

Studies should also be made of the consequences of the trend toward long cargo tanks and the probability of losing large quantities of cargo in event of collision. Studies might relate permissible wing cargo tank length to ship location, with respect to damage probability and limiting potential cargo loss. For example, published data exists which demonstrates that the greatest probability of collision damage exists in the forward half of the ship. Accordingly, a comparatively simple design compromise may be to require short tanks, on the order of (LBP/24 + 20), forward of amidships, and longer tanks, about 2 (LBP/24 + 20) aft of amidships.

Similar studies could also be made to establish minimum distance of the cargo tank section forward bulkhead from the forward end of the ship, and a minimum number of bulkheads between stem and cargo tanks, to provide a minimum standard of collision p otection. Such standards already exist in the rules of the classification societies, but modification may be justified following appropriate studies.

Grounding protection is normally provided by fitting of a double bottom in conventional dry cargo vessels. Except for the case of combination ore/oil or dry bulk/oil vessels where a double bottom is installed inboard of the longitudinal bulkheads, innerbottoms are not provided in tank vessels. Consideration could be given to such an installation, particularly inboard of the longitudinal bulkheads. This space could be used for clean

ballast, in much the same manner as the FORTUNA outboard wings, and the inner bottom designed to provide part of the effective longitudinal structure. Maximum protection would result with this arrangement in association with the FORTUNA wing tank arrangement. The economics of the double bottom is, however, less attractive than the FORTUNA wing tanks in terms of structural weight and cost.

As part of an arrangement study, standards could be established for bridge visibility, particularly in terms of line-of-sight over the bow. The standards should hold regardless of bridge location.

7.2.4 Structural Studies

Fundamental structural studies should be continued and/or initiated in the following areas:

- Continued study of longitudinal bending and improvement of estimating methods, with continued rational development of minimum standards.
- Study consequences of general scantling reductions which have been allowed through reduction of table scantlings and as a consequence of use of special coating systems. The extent that such reductions also reduce collision protection should be studied.
- Study modifications to structural design to increase collision protection. Outboard wings could be designed to absorb collision energy and limit penetration. Simple techniques are available to study various arrangements empirically, as in the case of collision protection structure provided outboard of the N.S. SAVANNAH reactor space.
- Associated with the above study, potential gains from use of higher strength steels could be considered.
- Consider the permanent installation of stress measuring instrumentation at strategic locations in the hull structure, with indicators located on the bridge. Continued development of simple devices to assist in determination of hull hog or sag bending moments will be of considerable value to the ship operators.

我中都があるからあるか、一年の日本の町本の一年の日本町であるからあって、ことのでは五月町までは、高からもの事業にある中華

A last resort means of stopping the ship, and a normal tool for low speed maneuvering, is the use of the ship's anchors. Progress in the development of ship's anchors has not kept pace with general ship technology, and

7-31

studies are suggested in the following areas:

• Develop more rapid means for release of anchor and chain. Centralized control of the mooring gear from the bridge has been provided in a few recent designs and is a step in this direction.

- Study problems involved in use of bow anchors in association with large bulbous bows. It is known that the anchors will glance off the bulb in some installations and the master is reluctant to use the anchor, short of an emergency. Consideration should be given to fitting of a stem-head anchor, similar to the arrangement adopted in certain naval ships of the DL, DLG or DE 1040 class.
- Study advisability of requiring the fitting of stern anchors, particularly in case of larger vessels, as an emergency stopping and maneuvering device and to facilitate maneuvering in congested waters.

7.2.6 Safety Requirements

Studies of tank vessel fire protection are likely to continue as a responsibility of the U.S. Coast Guard and the various regulatory bodies. Studies may be directed toward the following:

- Establishment of mandatory inerting requirements for normal use as well as for emergency measures.
- Study cargo pumping methods and piping systems with the object of establishing mandatory emergency cargo pumping systems. Methods of augmenting the normal pumping system as well as the mandatory installation of various fittings at each tank, to facilitate pumping from an attending ship, should be studied.
- Communication entire requirements for provision to mongency power sources to permit limited capability for cargo pumping in event of loss of the main plant.
- Navigation equipment. The development of improved radar, echo ranging, and depth sounding and recording is under continuous development and is well documented in the literature.

- Draft determination. Simple instrumentation could be developed to provide accurate forward, amidships, and after draft readings to the deck officers. These values are continuously changing during a voyage and such information becomes more important as ship sizes continue to increase.
- Whistle signals. The installation of visible signals to complement the audible whistle signals has been suggested as an aid to avoiding collisions and is, in fact, common practice on the U.S. Great Lakes.

7.2.7 Cargo Containment, in Event of Collision or Grounding

In addition to the obvious suggestion of requiring more and smaller tank compartmentation, various radical solutions have been suggested in public and private for containing or limiting the escape of liquid cargoes in the event of tank rupture. The following might be considered:

- Require the carriage of inflatable or other types of oil booms which would be secured to the ship in an arrangement to contain the oil slick.
- Development, and carriage aboard ship, of chemical detergent or other dispersal systems which could be sprayed by fire monitors or other devices on escaping oil at the surface, with the object of sinking the oil film to the sea bottom.
- Develop foamed plastic systems which could be released to temporarily seal off small ruptures in cargo tanks.

7.2.8 Radical Solutions

On a global basis, thought has been given to the following possibilities in limiting the pollution hazard:

- Restricting oil tanker operation to routes remote from populated areas or on comparatively lightly traveled ocean lanes.
- Adoption of costly navigation and/or inertial guidance systems to insure a higher precision in the control of ship routes.
- Use of submarine tankers, reducing the probability of ship collisions.

 The hazards of groundings are, of course, severely increased.
- Accelerated development of long distance oil pipelines as a substitute for tank vessels.

7.3 CONTROL OF OIL SPILLAGE

7.3.1 Surveillance

The potential of aerial photography and more especially infrared, ultraviolet, and microwave imagery in the surveillance and oil slick detection should be evaluated in detail. These techniques are all dependent on collecting reflected or emitted electromagnetic radiation from the surface and recording the intensity variations which are due to the reflective quality of the surface, temperature, and type of materials being observed. Various filtering systems should be evaluated to determine which portions of the ultraviolet and infrared spectrum would give the greatest oil-water contrast.

Because microwave imagery has all-weather capability, particular emphasis should be given to the development of this type of surveillance system. The first step would be an investigation of the response of the microwave imaging system to the oil-water surfaces. The microwave data which are collected on magnetic tape may be processed by techniques used on ultraviolet and infrared imagery which should enhance the microwave radiation intensity variations.

FM-CW radar has similar all-weather capability and should be ev luated along with the microwave imagery approach, but the latter should be given first priority.

Aerial reconnaissance techniques should also be considered to track surface buoys which could be released near the oil spill to determine the rates of surface currents. A combination of photographic, ultraviolet, infrared, and microwave imaging techniques should allow surface current measurements to be made under almost any weather condition and in a stort period of time.

7.3.2 Prediction of Oil Slick Behavior

The behavior and rate of movement of oil slicks on weder is rather poorly understood despite the importance in deploying defensive measures. Transport and dissipation are the two pertinent problems.

The direction and speed of an oil slick is expected to yield more to the wind than to the influence of the ocean current. This is because of the greater momentum transported to the oil slick by the wind. The wind and currents are very likely not in the same direction. Water currents near the surface which are under the influence of the wind are expected to follow the mathematical representation of the Ekman spiral. The wind created currents thus flow slightly to the right of the wind direction in the Northern Hemisphere. Mechanically and thermally induced ocean currents (i.e., Guif Stream) would affect the motion of an oil slick as well. As an oil slick approaches a land mass, a variation in the motion of an oil slick is also expected.

The dissipation of oil slicks would primarily rely on "storm" conditions. During periods of high wave and strong wind, the edges of the oil slick would be broken up and carried away. Water and atmospheric conditions could be related to this breakup. The area of initial breakup could be pin-pointed by using Eulerian coordinates or other suitable coordinate systems. The size of the oil slick and thickness at the center point may have additional bearing on the rate that an oil slick will break up, as well as the age of the oil slick.

It is proposed that a correlation of mean wind velocity at the surface and the mean velocity of the ocean current for various sizes of oil slicks could be related to the movement of the oil slick. Such a study could start with relatively small oil slicks. The resulting hypothesis could be extended to larger oil slicks. Assumptions that are made as the experiments progress (to larger oil slicks) could be tested.

An initial study of the breakup of oil slicks could be done by relating the breakup of small oil slicks to mean wind speed and wave size. This relationship could be extended to include fluctuations in the downwind and crosswind components of wind speed, and the changing characteristics of waves related to fetch length. Through photographs and/or infrared scanning of the oil slick taken by an aircraft flying over the test area, a study could be made on the rate of breakup and to determine the edge of the oil slick that breaks up first. Such studies could then be extended to the concurrent consideration of the parameters of net radiation; temperatures of the atmosphere, the oil, and the ocean; measurements of turbulence; and measurements of wave heights and character. Once the relation between these parameters and oil slick breakup is established, determination of a

portion or all of these parameters could provide additional information on the weakest area of an oil slick. Knowing this weak area, one could establish where the application of a detergent, and/or other additives or influences could be applied to permit natural forces to act to the best advantage in dispersion of an oil slick.

7.3.3 Chemical Treatment - Absorption

The use of absorbents in cleaning up oil spills should be carefully examined from the standpoint of objectives. For example, if the primary objective is economy without regard to potential oil reclamation, then it is very likely that a different absorbent would be used than if reclamation was the prime objective. The requirement of cleanup time should be factored into the formulation of objectives. If a relatively long period of time is available in which to undertake control measures, then a specific absorbent type might be more apparent.

The areas in which sunken oil-absorbent masses would create grave ecological problems should be defined so that appropriate control decisions can readily be made. The consequences of sunken oil-absorbent masses should be documented by a detailed research program.

Absorbent dispersal techniques should be examined. Priority should be given to those control methods which will be most effective when quick action is critical because of the limited extent of the affected area: 1, e, . aerial dispersal techniques.

It is also recommended that a test and evaluation program using standardized procedures be initiated to create some order out of the currently chaotic body of information.

Increased attention should also be given to the development of economical absorbents which meet predetermined criteria such as ease of spreading, ease of collection, and ease of oil reclamation or disposal.

7.3.4 Chemical Treatment - Dispersion

Although the general use of detergents is not recommended in this report, there are situations where such use is warranted. The major need at present is a test and evaluation program similar to that recommended for absorbents. In addition, standardized screening for biological toxicity and for biologicalability will be required.

BATTELLE NORTHWEST

The possibility of developing a nontoxic emulsifying agent should be explored from the biochemical standpoint as should the development of a detergent with shorter biodegradation half-life. These latter suggestions represent long-range goals.

7, 3, 5 Biological Degradation

The use of specific cultures of microbiological species which can rapidly metabolize oil should be investigated. Despite the fact that this has been suggested by numerous sources, there has been no field experimentation to demonstrate the practical application for oil spills. In any case, it is doubtful that this measure could be relied upon as the sole method for dissipating oil slicks which threaten land masses.

Methods for enhancing oxygen availability and nutrient supplies for accelerated microbial metabolism should be explored. Dispersal of nutrient materials and/or the mechanical or chemical addition of oxygen to the slick area should be examined in detail.

The mechanisms of anaerobic degradation of sunken oil masses should be investigated along with an assessment of potential toxicity of intermediate products of degradation. Likewise the effects of intermediate products (from aerobic environments) should be evaluated.

7.3.6 Rooming

Booming of oil spills has been a very effective method for containment of oil slicks in sheltered and relatively current-free waters. With the exception of a few commercial designs, the majority of booms have been of makeshift design using materials readily at hand. These have been generally ineffective largely due to lack of understanding of the hydraulics and dynamics involved.

It seems likely that by approximing boom design through careful consideration of the hydrodynamics and aerodynamics involved, it should be possible to develop the critical design criteria for a boom to be effective in comparatively high sea states. As a minimum, such criteria would include draft, freeboard, shape, particularly above the waterline, linear stresses, flexibility needs, inertia, and mooring forces. From this basis, several candidate designs could then be evolved, screened for feasibility in terms of materials, costs, deployability etc., and the more promising

designs evaluated in model basin tests. Should results prove favorable, one or more prototype booms could then be evaluated in field tests

The bubble curtain barrier warrants further evaluation and optimization. At the present time the limitations on its utility as a result of current and wave action are not known despite its mechanical simplicity and apparent merit. Should tests confirm its effectiveness, the design of a bubble curtain system capable of rapid deployment should be undertaken. There is an excellent possibility that improved performance can be achieved by optimizing submergence, air distribution, and bubble size to achieve maximum local upwelling of water and foam with a minimum of air supply. The addition of surfactants to the air supply, as is done in ore flotation processes, may greatly increase the air utilization efficiency, and this potential should be investigated.

Chemical booming, that is, the use of spreading agents, warrants further evaluation.

7.3.7 Skimming

All presently employed skimming vessels currently suffer from low rates of oil removal coverage or from inability to operate effectively in rough water. It appears likely, however, that an improved skimming device could be designed based on incorporation of several improvements. For example, the rotary drum (Earle)skimmer is relatively insensitive to wave action, but it is deficient in rate of removal. This latter drawback could possibly be overcome by (1) using a series of spaced discs rotating around a horizontal axis and (2) covering the surfaces of the discs with a hydrophobic oil absorbent foam. Roller type wringers would remove the absorbed and adherent oil from the disc surfaces with each revolution. Disc watered, Preliminary design of such a device is recommended.

7, 3, 8 Disposal of Recovered Slicks

It is readily apparent that the present methodologies used in treating recovered oil slicks could be materially aided by an information interchange with other areas of the total problem. For example, oil reclamation is a

topic which deserves far greater emphasis in the treatment of recovered slicks. Yet methods have been developed by those interested in removing slicks from the sea which could be directly applied to the recovery problem. If efforts are successful for enhancing biological degradation in the ocean, then similar techniques could be used for recovered slicks.

The weakest area in the disposal of recovered slicks is that of sludge disposal. Increased emphasis on environmental quality will dictate that improved sludge disposal techniques be developed.

Increased emphasis should also be placed on more effective oil reclamation throughout the treatment process. Improved primary separation offers the best possibility for such research.

7. 4 RESTORATION

The potential for developing improved detergents and emulsifiers has been previously mentioned, although use of these agents in beach and shoreface restoration is not generally recommended. It has also been pointed out that the restorative methods to be applied in a given situation are best decided on site. Further, mechanical removal of the oil is preferred where possible.

In this regard, the only research and development that appears warrented is an evaluation of the behavior, with time, of various types of crude oil and refined products on beaches: that is, weathering rates, rates of agglomeration with sand, penetration, etc. The information derived would have primary use in the development of contingency of plans rather than in actual restoration operations. For example, this information would permit advance estimates of the types and quantities of machinery and manpower required.

The use of absorbents and congealing agents may have considerable merit in preventing the penetration of relatively fresh oil into beach sands and shingle as well as in aiding its mechanical collection and removal. Various candidate materials should be evaluated in small-scale field tests with consideration given to local availability, cost, effectiveness, and ease of distribution and pickup. The use of demulsifiers in combating water-in-oil emulsions ("chocolate mousse") should also be explored.

Development of specialized equipment for removing oil from beaches does not appear warranted as the frequency of occurrence is low and existing earth-moving and agricultural machinery is generally adequate if not optimum.

7.5 EFFECTS

The survey of the literature on the biological and ecological effects following an oil spillage indicates that while some information is available on the damage that can occur, little quantitative and coherent data is available either to assess past incidents or to predict the potential effects in the future. Work currently being conducted in the United Kingdom may greatly augment the existing body of knowledge in the near future. In order to define water quality standards for oil and detergents under low level chronic situations and to assess the potential effects of large scale spillages, much more comprehensive data is required.

The major problem in attempting to define more precisely the effects of oil and control or restoration chemicals is the wide diversity in the physical and chemical composition of the products. The oil can vary from a crude to a refined petroleum product. The emulsifier can also be a complex mixture of detergent, dispersant, and solvent. The introduction of these substances into the sea, whether by accident or as part of a controlled cleanup operation results in a composition that will change with time, physically and chemically, by agitation due to wave action, by loss of volatile components, and by general weathering and biodegradation.

The literature would suggest, especially in the case of the TORREY CANYON episode, that oil itself appears to be comparatively harmless to most shore organisms. On the other hand, the detergents used in the clean-up were toxic, and those best at forming a stable emulsion were the most toxic. There is also evidence to suggest that the solvent phase of the detergent mixture was the toxic component.

While ultimately there will be a need for investigating the toxicity and effect of many such materials on a wide range of marine organisms, we recommend that immediate steps be taken to investigate the following problem areas:

Short-Term Acute Toxicity Tests

The relative sensitivities and lethal limits of the organisms to various oil products and emulsifier components should be established. Selected

organisms should include those important to the commercial shellfish and fishery industry.

Bioassay Techniques

A broad spectrum of bioassay techniques needs to be developed. These techniques will need to be standardized in order to allow intercomparison between geographical and ecological regions.

Depuration

Data on the degree of tainting and rate of loss needs to be established for shellfish. The economics of mass transportation of selected brood stocks to clean areas needs to be evaluated.

Biodegradation of oil and emulsifiers

Studies are required on the role and rate of degradation of pil products and emulsifier components by aquatic organisms, with emphasis on bacteria.

Long-Term Chronic Toxicity Tests

This phase of the studies should examine the clinical response of organisms to different sublethal concentrations (e.g. growth, fecundity, etc.) in order to better define water quality standards.

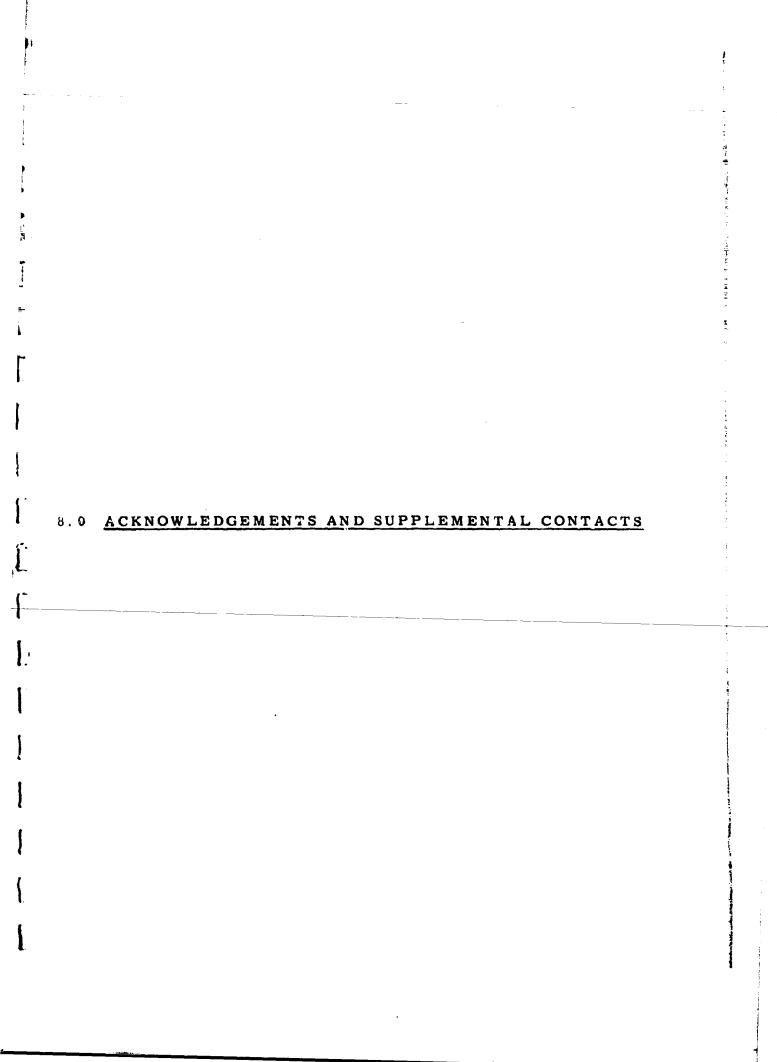
Biochemical and Physiological Studies

Selected physiological, biochemical, and behavioral studies as suggested from the short-term and long-term exposures should be initiated. Physiological studies could examine parameters such as repiration rates, photosynthesis, swim performance, osmotic balances and alteration in adaptation rate. Biochemical studies should relate alterations in metabolic processes with changes in cell ultrastructure. These multidisciplinary investigations would be aimed at establishing the biolog—1 basis for harmful effects to aid in understanding the toxicity syndrome.

Field Studies

These should be carried in selected areas on a controlled basis. Acute and long-term exposure studies should be conducted under natural conditions. Laboratory findings on the sensitivity of species must be verified by conducting similar studies under field conditions.

BATTELLE -- NORTHWEST



8.0 ACKNOWLEDGEMENTS AND SUPPLEMENTAL CONTACTS

8.1 ACKNOWLEDGEMENTS

Although much of the preceding discussion and recommendations have been derived from study of the formal literature, it was immediately apparent that a great deal of applied technology and art had been developed prior to the TORREY CANYON disaster, and that even more was developed immediately subsequent. Much of this information does not appear in the formal literature, and many of the experiences and lessons to be learned from the TORREY CANYON disaster still remain to be published.

Recognizing the above factors, numerous industrial organizations, Federal and State agencies, associations, and foreign sources were contacted, either personally or by letter. In almost all instances, helpful responses were obtained and with very gratifying results. As this report would be grossly incomplete without this input, these contributions are gratefully acknowledged. In some instances, identification of possible sources of information was not obtained early enough in the course of the study to permit follow-up. Similarly, although a concerted attempt has been made to cover all potential sources, there is no doubt that some have been inadvertently overlooked.

Special thanks are due to the following:

LCDR J. E. Bennett Office of Naval Research— London

Kenneth Biglane, Chief Enforcement Activities Section Federal Water Pollution Control Administration

W. C. Brodhead, Vice President Gulf Oil Company New York, NY

K. G. Brummage British Petroleum Company United Kingdom

Joseph M. Caldwell

Technical Advisor

Coastal Engineering Research Center
U.S. Army Corps of Engineers

M. Mac Earle
Surface Separat
Baltimore, Md

John B. Glude

Deputy-Regional Director

Bureau of Commercial Fisheries
Seattle, Wa

C. C. Hall, Director Warren Spring Laboratories Ministry of Technology United Kingdom

J. T. Higgins, Vice President Standard Oil Company of California

Capt. W. A. Jenkins Office of Law Enforcement U.S. Coast Guard

M. Mac Earle Surface Separators Systems, Inc. Baltimore, Md W. K. Miller, Director Office of Maritime Affairs Department of State National Oceanographic Data Center Washington, DC

Further sincere thanks are extended to the following people who contributed unpublished material for use in this report.

Dr. Max Katz Assistant Professor University of Washington College of Fisheries Seattle, Wa Dr. Albert K. Sparks Professor University of Washington College of Fisheries Seattle, Wa

Clyde S. Sayce Director Willapa Shellfish Laboratory Ocean Park, Wa Herb Tegelberg Chief, Razor Clam Operations Washington State Department of Fisheries Aberdeen, Wa

C. Dale Snow Chief, Shellfish Investigations Oregon Fish Commission Marine Research Center Newport, Or

8.2 SUPPLEMENTAL CONTACTS

Academic and Institutional

University of Alaska Institute 6. Marine Science College, Ak 99735

Arctic Research Laboratory Point Barrow, Ak 99723

Bears Bluff Laboratories Wadmalaw Island, SC 29487

Bermuda Biological Station St. George's West, Bermuda

California Academy of Sciences Golden Gate Park San Francisco, Ca 94118

University of California Institute of Marine Resources Scripps Institute of Oceanography P.O. Box 109 La Jolla, Ca 92037

University of California at San Diego Scripps Institution of Oceanography La Jolla, Ca 92038 University of California at Santa Barbara Department of Biological Sciences Santa Barbara Marine Station Santa Barbara, Ca 93106

California Institute of Technology Kerchoff Marine Laboratory 101 Dahlia St. Corona del Mar, Ca 92625

Catalina Marine Biological Laboratory Fisherman Cove Santa Catalina Island, Ca 91106

Cape Haze Marine Laboratory 9501 Bling Pass Rd. Sarasota, Fl 33581

College of Charleston Marine Biological Laboratory Charleston, SC 29203

Columbia University Geophysical Field Station St. David's, Bermuda

BATTELLE NORTHWEST

Columbia University Lamont Geological Observatory Palisades, NY 10964

Columbia University Hudson Laboratories 145 Palisade St. Dobbs Ferry, NY 10522

University of Connecticut Marine Research Laboratory Storrs, Ct 06268

University of Delaware Marine Laboratories Department of Biological Sciences Newark, De 19711

University of Delaware Marine Laboratories Bayside Laboratory P.O. Box 514 Lewes, De 19958

Duke University Marine Laboratory Beauford, NC 28516

Eastern Shore Laboratory Wachapreague, Va 23480

University of Florida Marine Laboratory Cedar Key, Fl 32625

University of Florida College of Engineering Coastal Engineering Department Gainsville, Fl 32603

Florida State University Oceanographic Institute Tallahassee, Fl 32306

Fort Johnson Marine Biological Laboratory Rt. 1 Charleston, SC 29407

University of Georgia Marine Institute Sapelo Island, Ga 31327

Gulf Coast Research Laboratory Ocean Springs, Ms 39564 University of Hawaii Hawaii Marine Laboratory Honolulu, Hi 96814

Harvard University Museum of Comparative Zoology Cambridge, Ma 02138

Humboldt State College Laboratory Arcata, Ca 95521

Institute of Oceanography and Marine Biology
P. O. Box 432
Gyster Bay, L. I. NY 11771

Inter-American Tropical Tuna Commission Headquarters Laboratory c/o Scripps Institution of Oceanography La Jolla, Ca 92037

Inter-American Tropical Tuna Commission Terminal Island Laboratory 700 Tuna St. Terminal Island, Ca 90731

International Pacific Halibut Commission c/o University of Washington Fisheries Hall No. 2 Seattle, Wa 98105

Johns Hopkins University Baltimore, Md 21218

Johns Hopkins University Chesapeake Bay Institute Oceanography Building Baltimore, Md 21218

Lehigh University Marine Science Center Bethlehem, Pa 18015

Lerner Marine Laboratory Bimini, Bahamas B.W.L

Louisiana State University Coastal Studies Institute Baton Rouge, La 70803 University of Maine Marine Station ira C. Darling Center for Research, Teaching and Science Walpole, Me 04573

Massachusetts Institute of Technology Department of Geology and Geophysics Department of Meteorology and 54-912 Earth Science Laboratory 77 Massachusette Ave. Cambridge, Ma 02139

Marine Biological Laboratory Woods Hole, Ma 02543

University of Maryland Natural Resources Institute Chesapeake Biological Laboratory P.O. Box 38 Solomons, Md 20688

University of North Carolina Institute of Fisheries Research Morehead City, NC 28557

Oceanographic Institute Marine Laboratory Crawfordville, Fl 32327

Oregon State University Corvallis, Or 97331

Oklahoma State University Stillwater, Ok 74074

New Jersey Oyster Research Laboratories Rutgers Shellfish Laboratory 128 Ocean Ave. Monmouth Beach, NJ 07750

New Jersey Oyster Research Laboratories RFD #2 Cape May Courthouse, NJ 08210

New Jersey Oyster Research Laboratories Department of Zoology, Rutgers The State University New Brunswick, NJ 08903

New Jersey Oyster Research Laboratories, Department of Zoology, Rutgers, Oyster Research Laboratory The State University Bivalve, NJ 08301

New York University Oceanography School of Engineering and Science University Heights Bronx, NY 10453

Oceanic Institute Makapuu Point, Oahu, Hi 96700

Oregon State University Marine Science Laboratory Box 15? Newport, Or 97365

University of Oregon Oregon Institute of Marine Biology Charleston, Or 97420

Pacific Science Center Foundation 4000 NE 41st St. Seattle, Wa 93105

Pacific Union College Mendocino Biological Field Station Albion, Ca 95410

University of the Pacific Pacific Marine Station — Dillon Beach, Ca 94929

Philadelphia Academy of Natural Department of Limnology Philadelphia, Pa 19003

. .

University of Puerto Rico Institute of Marine Biology Mayaquez, Puerto Rico 00708

University of Rhode Island Narragansett Marine Laboratory Graduate School of Oceanography Kingston, RI 02881

University of Southern California Allan Hancock Foundation University Park Los Angeles, Ca 90007

University of Southwestern Louisiana Lafayette, La 70801

Stanford University Hopkins Marine Station Pacific Grove, Ca 93950

Texas A&M University
Department of Oceanography
College Station, Tx 77843

Texas A&M University
Marine Research Laboratory
Galveston, Tx 77550

University of Texas Institute of Marine Science Port Aransas, Tx 78373

University of Texas
Texas Petroleum Research
Committee
201 Petroleum Engineering
Building
Austin, Tx 78712

Tiburon Oceanographic Institute
Box 647
Tiburon, Ca 94920

Trident Research Facility Tudor Hill, Bermuda

Virginia Institute of Marine Science Gloucester Point, Va 23062

Walla Walla College Biological Station Anacortes, Wa 98221

University of Washington 15th Ave. NE&NE 40th Seattle, Wa 98105

University of Washington College of Fisheries Library Seattle, Wa 98105 University of Washington College of Fisheries Seattle, Wa 98105

University of Washington Friday Harbor Laboratory Friday Harbor, Wa 98250

Western Washington State College Department of Biology Bellingham, Wa 98225

Woods Hole Oceanographic Institution Woods Hole, Ma 02543

Yale University Bingham Oceanographic Laboratory Box 2025 Yale Station New Haven, Ct 06520

Equipment Manufacturers

Allis-Chalmers Milwaukee, Wi 53201

American Well Works Aurora, Il 60507

Beckman Instruments, Inc. Fullerton, Ca

Bowser-Briggs Filtration Division Cooksville, Tn

Can-Tex Industries, Inc. Mineral Wells, Tx 76067

Ralph B. Carter Company Hackensack, NJ

Combustion Engineering, Inc. Chicago, Il

Crane Company Chicago, Il

Dorr-Oliver, Inc. Stanford, Ct

The Eimco Corporation Salt Lake City, Ut

Fischer and Porter Company Warminster, Pa 18974

Foxboro Company Foxboro, Ma 02035

General Electric Company Schenectady, NY

Georgia-Tennessee Mining & Chemical Company Wresso, Ga

B. F. Goodrich Industrial Products Company Marietta, Oh

Hardinge Company York, Pa

Honeywell, Inc. Fort Washington, Pa 19034

Inertol Company Newark, NJ

INFILCO/GATX Tucson, Az

ITEC Corporation
Data Analysis Center
616 Franklin Strect
Alexandria, Va. 22314

Johns-Mansville Sales Corporation New York, NY

Komline-Sanderson Engineering Corporation Peapack, NJ 07977

Lakeside Engineering Corporation Chicago, Il

F. B. Leopold Company Zelienople, Pa 16063

Link-Belt Company Comar, Pa

National Water Main Cleaning Company Chicago, Il The New York Air Brake Company Providence, RI

Nichols Engineering and Research Corporation New York, NY

Pacific Flush Tank Company Chicago, Il

Permutit Company East 49 Midland Ave. Paramus, NJ 07652

Petrolite Corporation 1300 Rock Ave. East Apartment L-1 North Plainfield, NJ 07060

Petrolite Corporation Box 2546 Houston, Tx 77001

Smith and Loveless Leneva, Ks 66215

Southwestern Engineering Company Los Angeles, Ca

. .

Surface Separator Systems, Inc. 103 Mellor Ave. Baltimore, Ma 21228

Wallace and Tiernan, Inc. Belleville, NJ 07109

Walker Process Equipment, Inc. Aurora, Il

Walter Kidde Company Belleville, NJ 07109

Wells Products, Corporation Roscoe, 11 61073

Yeomans Brothers Company Melrose Park, Il

Petroleum Industry

American Oil Company Whiting, In 46394

American Petroleum Company Seattle, Wa

Chevron Research Corporation Richmond, Ca

Chevron Research Corporation Box 446 La Habra, Ca 90631

Chevron Shipping Company 225 Bush St. San Francisco, Ca 94104

Cities Service Tanker Corporation 60 Wall Street New York, NY 10005

Cities Service Research Cranbury, NJ 08512

Esso Tankers, Inc. Humble Oil and Refining Company 800 Bell Ave. Houston, Tx

Gulf Oil Corporation 1290 6th Ave. New York, NY 10029

Humble Oil Company Coordinator of Oil and Water Pollution Houston, Tx

Keystone Shipping Company Philadelphia, Pa

Shaver Transportation Company 4900 NW Front Ave. Portland, Or 97210

Shell Development Company 50 West 50th St. New York, NY 10020

Shell Development Company 1400 53rd St. Emeryville, Ca 94608

Sinclair Refining Company 410 E. Sibley Blvd. Harvey, II 60426 Socony Mobil Oil Co Washington, DC

Standard Oil of California 225 Bush St. San Francisco, Ca 34104

Standard Oil of Kentucky Box 1300 Pascagoula, Ms 39567

Sun Oil Company Philadelphia, Pa

Texa Inc.
Marine Department
125 E. 42nd St.
New York, NY 10017

Chemical Industry

Dow Chemical Company Midland, Mn 48640

Gamlin Chemical Company 321 Victory Avenue South San Francisco, Ca 94080

Hercules, Inc. Wilmington, De

Magnus Chemical Company 400 So. Ave. Garwood, NJ 07087

Nalco Chemical Company Chicago, 11

Norad Industries, Inc. Sangatuck, C1 06882

Oceanwide Marine Supply Company Box 827 Huntington Long Island, NY 11743

Pluess-Staufer (North American) 82 Beaver St. New York, NY 10005

Sterling Drug Company Rothchild, Wi 51474

Foreign

Admiralty Oil Laboratory Brentford Middlesex, England

Admiralty Materials Laboratory Dorset, England

Audobon Society of Canada 46 St. Clair Ave. East Toronto 7, Canada

Battelle-Institute e. V. Wiesbadwerstosse 6 Franfurt/Main, W 13 Germany

The Bristol Airplane Plastics, Ltd. Sultan
Bristol, England

The British Petroleum Company Brittanic House Moor Lane London, E.C. 2 England

Bundesanstalt Fuer Gewasserkunde (Liaison Office for Hydrology) Kaiserin-Augusta-Anlagen 15 54 Koplenze Germany

Department of Northern Affairs and National Resources Ottawa, Canada

Canadian Wildlife Service St. Johns, Newfoundland Canada

Deutscher Arbeitskreis Wasserforschung, e. V. Rochusstr. 36 40 Dusseldorf Germany

The British Trust for Ornithology 91 Banbury Road Oxford, England Directorate of Materials Research Royal Navy, Ministry of Defense Main Building, Whitchall London, England

Directorate of Marine Services (Salvage) Ministry of Defense Main Building Whitehall London, England

University of Durham Botany Department Durham, England

Ente Nazionale Idrocarburi Via Dell-Arte Rome, Italy

The European Federation for the Protection of Waters c/o Lique Suisse pour la Protection des Eaux Kuerbergstr. 19
Zurich 10/49, Switzerland

Government Industrial Research Institute, Osaka Agency of Industrial Science and Technology Ministry of International Trade and Industry 1-9-1, Kita, Oyodo-cho, Yodo-ku Osaka, Japan

Hydraulics Research Station Wallingford, England

Intergovernmental Maritime Consultative Organization Chancery House Chancery Lane London, W. C. 2, England

M.A.F.F. Fisheries Research Laboratory Lowestoft Suffolk, England

; .

M. A. F. F. Shellfish Research Laboratory Burnham on Crouch Essex, England

Marine Biological Association U. K. Citadel Hill Plymouth, Devon England

Maritime Safety Agency Ministry of Transportation, 2-1, Kasumigaseki, Chiyoda-ku, Tokyo, Japan

Ministerio de Hacieda Administration General de Los Sercinos Portuorios Nacionalis Caracas, Venezuela

Ministry of Power Thames House South Milbank London, SW 1, England

Ministry of Technology Warren Spring Laboratory Gunnels Wood Road Stevenage, Hertfordshire England

National Environmental Research Council State House High Holborn London, W.C. 1, England

The Nature Concervancy England

Netherland Institute for Fishery Investig tions Haring Kade 1 P. O. Box 68 Ijmuiden, Holland Research Promotion Section Research Coordination Bureau Science and Technology Agency 3, 4, Kasumigasek! Chiyoda-ku, Tokyo, Japan

Royal Navy Ministry of Defense Main Building Whitehall, London

Rotterdam Port Authority Rotterdam, Netherlands

Royal Society for the Protection of Birds The Lodge, Sandy Bedfordshire, England

Sealight Manufacturing Company, Ltd. Kyodo Building, 1-1 Hon-machi, Nihonbashi, Chuo-ku, Tokyo, Japan

The Secretary
The Royal Society for the Protection
of Birds
82 Victoria St.
London SW-1
England

Ship Research Institute Ministry of Transportation, 1-3-8, Mejiro, Toshima-ku, Tokyo, Japan

Sumitoma Denko Kogyo Company, 1.td. Sanyu Building, Shiba-Kotohira, Minato-ku, Tokyo, Japan

University of London Chelsen College of Technology Department of Pharmacy London, England

William Warne and Company, Ltd. Barking Essex, England

Federal Agencies

Department of Commerce

Maritime Administration Office of R&D Office of Ship Construction Division of Ship Design Washington, DC

Library of Congress

National Referral Center for Science and Technology Library of Congress Annex Building Washington, DC 20540

Department of Defense

- U.S. Army Corps of Engineers Coastal Engineering Research Center 5201 Little Falls Road NW Washington, DC 20016
- U.S. Army Corps of Engineers Walla Walla District City-County Airport Walla Walla, Wa 99362
- U.S. Army Corp of Engineers
 Board of Engineers for Rivers and
 Harbors
 Port Statistics Branch
 New Orleans, La
- U.S. Army Corp of Engineers Vicksburg District Vicksburg, Ms 39181
- U.S. Army Office of the Chief of Engineers Permanent International Association of Navigational Congresses Board of Rivers and Harbors Washington, DC 20315
- U.S. Army Office of the Chief of Engineers Engineering Division Washington, DC 29315

U.S. Navy Military Sea Transport Service Tanker Division Transport and Tanker Eng. Div. Washington, DC

National Oceanographic Data Center Washington, DC 20390

Naval Research Laboratory Washington 25, DC

Office of Naval Research-London Box 39, FPO New York, NY 09510

Office of Naval Research Washington, DC

- U.S. Naval Oceanographic Office Coastal Oceanography Unit Code 7250 Washington, DC 20390
- U.S. Naval Oceanographic Office Research and Development Department Code 7001 Washington, DC 20390

: -

Naval Ship Engineering Center Environmental Control Section, Chemical Cleaning Branch Main Navy Building Washington, DC 20360

Department of Meteorology and Oceanography U.S. Navy Postgraduate School Monterey, Ca 93940

Norfolk Naval Air Station Oceanographic Services Office Norfolk, Vi 23511

U.S. Navy Ships Systems Command Chief of Salvage Main Navy Building Washington, DC 20360

Executive

東京の大学の大学の大学の大学の大学の大学を大学

National Council on Marine Resources and Engineering Development Washington, DC

Department of State
Office of Maritime Affairs
Washington, DC 20520

U.S. Public Health Service Bethesda, Md

Bureau of Commercial Fisheries Radiobiological Laboratory Pivers Island, Beaufort, NC 28516

Bureau of Commercial Fisheries Biological Laboratory P.O. Box 3830 Honolulu, Hi 96812

Bureau of Commercial Fisheries Biological Laboratory P.O. Box 155 Auke Bay, Ak 99821

Bureau of Commercial Fisheries
Biological Field-Station
P.O. Box 438
Tiburon, Ca 94920

Bureau of Commercial Fisheries Ichthyological Field Station North Rotunda, Museum Building Stanford, Ca 94305

Bureau of Commercial Fisheries Biological Laboratory 450-B Jordan Hall Stanford, Ca 94305

Bureau of Commercial Fisheries Tuna Resources Laboratory P.O. Box 271 La Jolla, Ca 92038

Bureau of Commercial Fisheries California Current Resources Laboratory Fishery-Oceanography Center P. O. Box 271 La Jolla, Ca. 92038 Bureau of Commercial Fisheries Biological Laboratory Building 302 Ft. Crockett Galveston, Tx 77552

Bureau of Commercial Fisheries Statistics and Market News Statistical Center Rooms 609-611 Federal Building 600 South St. New Orleans, La 70130

Bureau of Commercial Fisheries Biological Laboratory Sabine Island Gulf Breeze, Fl 32561

Bureau of Commercial Fisheries Biological Station 75-33rd Ave. St. Petersburg Beach, Fl 33706

Bureau of Commercial Fisheries Tropical Atlantic Biological Laboratory 11 Rickenbacker Causeway 2 mi, F1 33149

Bu eau of Commercial Fisheries Biological Laboratory P.O. Box 280 Brunswick, Ga 31521

Bureau of Commercial Fisheries Biological Laboratory Pivers Island Beaufort, NC 28516

Bureau of Commercial Fisheries Biological Laboratory Oxford, Md 21654

Bureau of Commercial Fisheries Biological Field Station Building 74 Navy Yards Annex Washington, DC 20390

Bureau of Commercial Fisheries Biological Laboratory Milford, Ct. 06460

BATTELLE NORTHWEST

Bureau of Commercial Fisheries Biological Laboratory P.O. Box 267 Boothbay Harbor, Me 04538

Bureau of Commercial Fisheries Biological Laboratory P. O. Box 6 Woods Hole, Ma 02543

Bureau of Commercial Fisheries Shellfish Pesticide Laboratory Gulf Breeze, Fl 32561

Bureau of Commercial Fisheries Branch of Resource Management Washington, DC 20240

Bureau of Commercial Fisheries Division of Biological Research Washington, DC 20240

Bureau of Mines Department of The Interior Washington, DC 20240

Sandy Hook Marine Laboratory Bureau of Sport Fisheries and Wildlife Fort Hancock Highland, NJ 07732

Federal Water Pollution Control Administration 633 Indiana Ave. NW Washington, DC 20004

Marine Geology and Hydrology Laboratory U.S. Geological Survey 345 Middlefield Rd. Menlo Park, Ca 94025

Office of Oil and Gas
U.S. Department of the Interior
Washington, DC 20240

U.S. Fish and Wildlife Service 6116 Arcade Building Seattle, Wa 98101

Other

Bethelehem Steel Corporation Sparrows Point Yard Sparrows, Md 21219

National Academy of Sciences Committee on Oceanography Ship Hull Research Committee Maritime Transportation Board Washington, DC

U.S. Coast Guard Station Newport, Or 97365

U.S. Coast Guard 1300 E. St., NW Washington, DC 20591

U.S. Coast Guard 1330 E. St., NW Washington, DC 20591

U.S. Coast Guard Maritime Safety Division 919 18th St., NW Washington, DC 20006

Coast Oyster Company Eureka, Ca 95501

Marine Digest Publishing Company 79 Columbia St. Seattle, Wa 98104

World Wide Divers, Inc. 6304 Alder Houston, Tx

Associations

American Association of Port Authorities 601 Southern Building 15th and H St. Washington, DC 20005

American Bureau of Shipping 45 Broad St. New York, NY 10004 American Humane Education Society 180 Longwood Avenue Boston, Ma 02115

American Iron and Steel Institute 150 East 42nd St. New York, NY 10017

American Petroleum Institute Division of Transportation 1101 17th St. NW Washington, DC 20036

American Petroleum Institute 1271 Avenue of the Americas New York, NY 10020

American Society for Microbiology Section on Aquatic Microbiology Institute of Marine Science University of Miami Rickenbacker Causeway Miami, Fl 33149

American Shore and Beach Preservation Association P. O. Box 1246 Rockville, Md 20850

Lake Carriers Association 305 Rockefeller Building Cleveland, Oh 44113

Maine Petroleum Association

National Audubon Society 1130 Fifth Ave. New York, NY 10028

National Petroleum Refiners Association Suite 802 1725 De Sales St., NW Washington, DC 20036

National Wildlife Federation Conservation and Education Division 1412 16th St., NW Washington, DC 20036 National Security Industrial Association Ocean Science and Technology Advisory Committee 1725 Eye St., NW Suite 208 Washington, DC 20006

Smithsonian Institution Science Information Exchange 1730 M St., NW Washington, DC 20036

Smithsonian Institution
Office of Oceanography and Limnology
Washington, DC 20560

Soap and Detergent Association 295 Madison Ave. New York, NY 10017

Society for Prevention of Cruelty to Animals Washington, DC

U.S. Salvage Association, Inc. 99 John St. New York, NY 10038

State Agencies

Alabama Fish and Game Commission Dauphin Island, Al 36528

Alabama Marine Resources Laboratory P.O. Box 188 Dauphin Island, Al 36528

Alaska Department of Fish and Game Box 350 Juneau, Ak 99801

Alaska Department of Fish and Game Kitoi Bay Research Station Kodiak, Ak 99615

California State Department of Fish and Game Laboratories Marine Resources Laboratory Hopkins Marine Station Pacific Grove, Ca. 93950 California State Department of Fish and Game Laboratories Marine Resources Operation Laboratory 411 Burgess Dr. Menlo Park, Ca 94025

California State Department of Fish and Game Laboratories Marine Resources Laboratories 127 G St. Eureka, Ca 95501

California State Department of Fish and Game Laboratories State Fisheries Laboratory 511 Tuna St. Terminal Island Station San Pedro, Ca 90731

California State Water Pollution Control Board Room 316 1227 O St. Sacramento, Ca 95814

Florida State Board of Conservation Salt Water Fisheries Division Marine Laboratory P.O. Drawer F St. Petersburg, Fl 33731

Division of Fish and Game
Department of Land and Natural
Resources
400 S. Beretania St.
Honolulu, Hi 96813

Louisiana Geological Survey Box G. Geology Building University Station Baton Rouge, La 70803

Louisiana Wildlife and Fisheries Commission Rockefeller Wildlife Refuge Laboratory Grand Chenier, La 70643

Louisiana Wildlife and Fisheries Commission Grande Terre Island 400 Royal St. New Orleans, La 70130 Oregon Fish Commission Research Laboratories Ri. 2, Box 31-A Clackamas, Oregon 97015 Branch Office; 855 Olney Ave. Astoria, Or 97103

Shellfish Laboratory
P.O. Box 157
Newport, Oregon 97635
Branch Offices:
P.O. Box 529
Charleston, Or 97420
P.O. Box 392
Oakridge, Or 97463

Maine Department of Sea and Shore Fisheries, State House August, Me 04330

٠.

Maine Department of Sea and Shore Fisheries Fisheries Research Station Boothbay Harbor, Me 04538

Mississippi Oil and Gas Board P.O. Box 1322 Jackson, Ms 39205

Oregon Fish Commission Marine Science Drives Newport, Or 97365

Marine Laboratory Texas Parks and Wildlife Department P.O. Box 1117 Rockport, Tx 78382

Washington State Department of Fish and Game Shellfish Nachotta, Wa 98637

Washington State Department of Fisheries Coastal Research Laboratories 401 W. Wishkah St. Aberdeen, Wa 98520 Washington State Department of Fisheries Fisheries Research and Management Branch Director Shellfish Research Branch Room 115, General Administration Building Olympia, Wa 98502

Port Authorities

Board of Harbor Commissioner P.O. Box 570 Long Beach, Ca 90801

Board of Harbor Commissioners P.O. Box 151 San Pedro, Ca 90733

Cleveland Port Authority 101 Eric Side Ave. Cleveland, Oh 44114

Delaware River Port Authority P.O. Box 1949 Camden, NJ 18101

Great Lakes Commission Director of Research 5104 1st Building, North Campus Ann Arbor, Mn 48105

Los Angeles Department of Water and Power P.O. Box 111 Los Angeles, Ca 90005

Maine Port Authority Maine State Pier Portland, Me 04111

Maryland Port Authority Director of Port Operations Pier, 2 Pratt St. Baltimore, Md 21202

New Hampshire State Port Authority 555 Market St. Portsmouth, New Hampshire 03801 Norfolk Port and Industrial Authority 1500 Maritime Tower Norfolk, Va 23510

Port of Beaumont P.O. Drawer 3626 Beaumont, Tx 77704

Port of Corpus Christi P.O. Box 1541 Corpus Christi, Tx 78403

Port Everglades Authority Port Everglades, Fl 33316

Port of Houston P.O. Box 2562 Houston, Tx 77001

Port of Oakland 66 Jack London Square Oakland, Ca 94607

The Port of Portland Commission P. O. Box 3529
Portland, Or 97208

The Port of New York Authority 111 Eight Ave. New York, NY 10011

Puerto Rico Ports Authority P.O. Box 3508 San Juan, Puerto Rico 00904

Port of Scattle P.O. Box 1209 Seattle, Wa 98111

San Diego Unified Port District 3165 Pacific Highway San Diego, Ca 92101

Saint Lawrence Seaway Development Corporation Seaway Circle Messena, NY 13662

1

ADDENDA

Associations

American Merchant Marine Institute 11 Broadway New York, NY 10004